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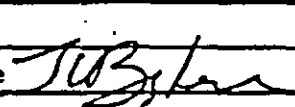


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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management



**United States
Department of Energy**
P.O. Box 550
Richland, Washington 99352

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Assistant Secretary for Environmental Management



**United States
Department of Energy**
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TERMS

CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CMS	corrective measures study
DOE	Department of Energy
EBF	electromagnetic borehole flowmeter
Ecology	Washington Department of Ecology
EDS	energy dispersive spectroscopy
EDTA	ethylenediaminetetraacetic acid
EPA	U.S. Environmental Protection Agency
ERA	ecological risk assessment
FT-IR	Fourier transform-infrared spectroscopy
gpm	gallons per minute
HRTEM	high resolution transmission electron microscopy
ICP	inductively coupled plasma
ISRM	in situ redox manipulation
ITRD	Innovative Treatment and Remediation Demonstration
LFI	limited field investigation
LSC	liquid scintillation counting
LWDF	liquid waste disposal facility
MNA	monitored natural attenuation
NPL	National Priorities List
OU	operable unit
PNNL	Pacific Northwest National Laboratory
PPE	personal protective equipment

ppm	parts per million
PRB	permeable reactive barrier
pv	pore volume
QRA	qualitative risk assessment
RAO	remedial action objective
ROD	Record of Decision
SNL	Sandia National Laboratory
⁹⁰ Sr	strontium-90
TAG	Technical Advisory Group
TDS	total dissolved solids
TTP	Treatability Test Plan
WIDS	Waste Information Data System
XRD	X-ray powder diffraction

1.0 INTRODUCTION

Efforts to reduce the flux of strontium-90 (^{90}Sr) to the Columbia River from past-practice liquid waste disposal sites have been underway since the early 1990s in the 100-N Area at the Hanford Site (Figure 1-1). Termination of all liquid discharges to the ground by 1993 was a major step toward meeting this goal. However, ^{90}Sr adsorbed on aquifer solids beneath the liquid waste disposal sites and extending to beneath the near-shore riverbed remains as a continuing source to groundwater and the Columbia River.

The remedy specified in the 100-NR-1/2 Interim Action Record of Decision (Ecology, 1999) included operation of a pump-and-treat system as well as a requirement to evaluate alternative ^{90}Sr treatment technologies. It was recognized from the onset that pump-and-treat was unlikely to be an effective long-term treatment method because of the geochemical characteristics of ^{90}Sr , the primary contaminant of concern. Subsequent performance monitoring has substantiated this expectation. Accordingly, the first Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) 5-year review re-emphasized the need to aggressively pursue alternative methods to reduce impacts on the Columbia River.

With the presentation of the *Evaluation of ^{90}Sr Treatment Technologies for the 100 NR-2 Groundwater Operable Unit* (Letter Report; Fluor/CH2M HILL, 2004) at the December 8, 2004, public meeting, U.S. Department of Energy (DOE), Fluor, Pacific Northwest National Laboratory (PNNL), and the Washington Department of Ecology (Ecology) agreed that the long-term strategy for groundwater remediation at 100-N will include apatite sequestration as the primary treatment, followed by a secondary treatment, or polishing step, if necessary (most likely phytoremediation). Since that time, the agencies have worked together to agree on which apatite sequestration technology has the greatest chance of reducing ^{90}Sr flux to the river, for a reasonable cost. In July 2005, aqueous injection, (i.e., the introduction of apatite-forming chemicals into the subsurface) was endorsed as the interim remedy and selected for field testing. Plans are underway to assess the capability of aqueous injection to address both the vadose zone and the shallow aquifer along the 300 feet of shoreline where ^{90}Sr concentrations are highest. This area is adjacent to the location where the pump-and-treat extraction well capture zone is closest to the N-springs shoreline (i.e., extraction wells 199-N-103A and 1-99-N-75, Figure 1-2A).

This Treatability Test Plan (TTP) provides the background for this decision, a description of the technology, and a general description of the treatability testing that will be conducted. Prior to field deployment of each phase of the treatability test, a set of detailed field test instructions will be developed. These instructions will incorporate results from ongoing laboratory experiments and design analysis simulations and provide a complete description of field test operational parameters and procedures.

Figure 1-1
100-N AREA, HANFORD SITE, WASHINGTON
100-NR-2 OPERABLE UNIT



This document is organized as follows:

Section 1: Introduction provides background, site description, nature and extent of ^{90}Sr contamination, regulatory history, summary of technology selection, and path forward.

Section 2: Treatment Technology Description describes the general characteristics of apatite and mineral apatite; the aqueous injection technique; discusses potential chemical effects of this treatment; and describes the testing that has been done using this technology.

Section 3: Bench-Scale Testing of Aqueous Injection describes bench tests conducted at SNL and at PNNL to demonstrate the feasibility of aqueous injection, and to quantify various processes involved in the technology.

Section 4: Field Test Plan for Aqueous Injection provides the test objectives and conceptual design and discusses site-specific characterization, flow and reactive transport simulations, previous modeling studies, and field test specifications.

Section 5: Schedule provides a general schedule for conducting the pilot test and installing up to a 300-foot barrier.

Section 6: References lists the documents used in writing this TTP.

1.1 Background

The Hanford Site is a DOE site located in southeastern Washington State near Richland, Washington. The 100-N Area is located along the Columbia River and includes the 100-N Reactor, a DOE nuclear reactor previously used for plutonium production.

The operation of the 100-N Area nuclear reactor required the disposal of bleed and feed cooling water from the reactor's primary cooling loop, the spent fuel storage basins, and other reactor-related sources. Two crib and trench liquid waste disposal facilities (LWDFs) were constructed to receive these waste streams, and disposal consisted of percolation into the soil. The first LWDF (1301-N) was constructed in 1963, about 244 meters (800 feet) from the river (Figures 1-2A and 1-2B, and see Figure 1-12). Liquid discharges to this facility contained radioactive fission and activation products, including cobalt-60, cesium-137, ^{90}Sr and tritium. Minor amounts of hazardous wastes such as sodium dichromate, phosphoric acid, lead and cadmium were also part of the waste stream. When ^{90}Sr was detected at the shoreline, disposal at the first LWDF was terminated and a second crib and trench (1325-N LWDF) was constructed farther inland in 1983. Discharges to 1325-N ceased in 1991.

A more complete history of the groundwater contamination at 100-N can be found in the *Hanford 100-N Area Remediation Options Evaluation Summary Report* (TAG, 2001). In summary, as a result of wastewater disposal practices, soils beneath the LWDFs were contaminated from the surface sediments to the lower boundary of the unconfined aquifer. A portion of the contaminants migrated to the Columbia River via groundwater. To address contamination in the 100-N Area, it was divided into two operable units (OUs). The 100-NR-1 OU contains all the source waste sites located within the main industrial area around the 100-N Reactor and the Hanford Generating Plant, and includes the surface sediments and shallow subsurface soil associated with the LWDFs. Remedial activities that address the contamination in this unit are ongoing. 100-NR-2 contains the contaminated groundwater and aquifer.

Figure 1-2A. Plot Plan Showing Site Features

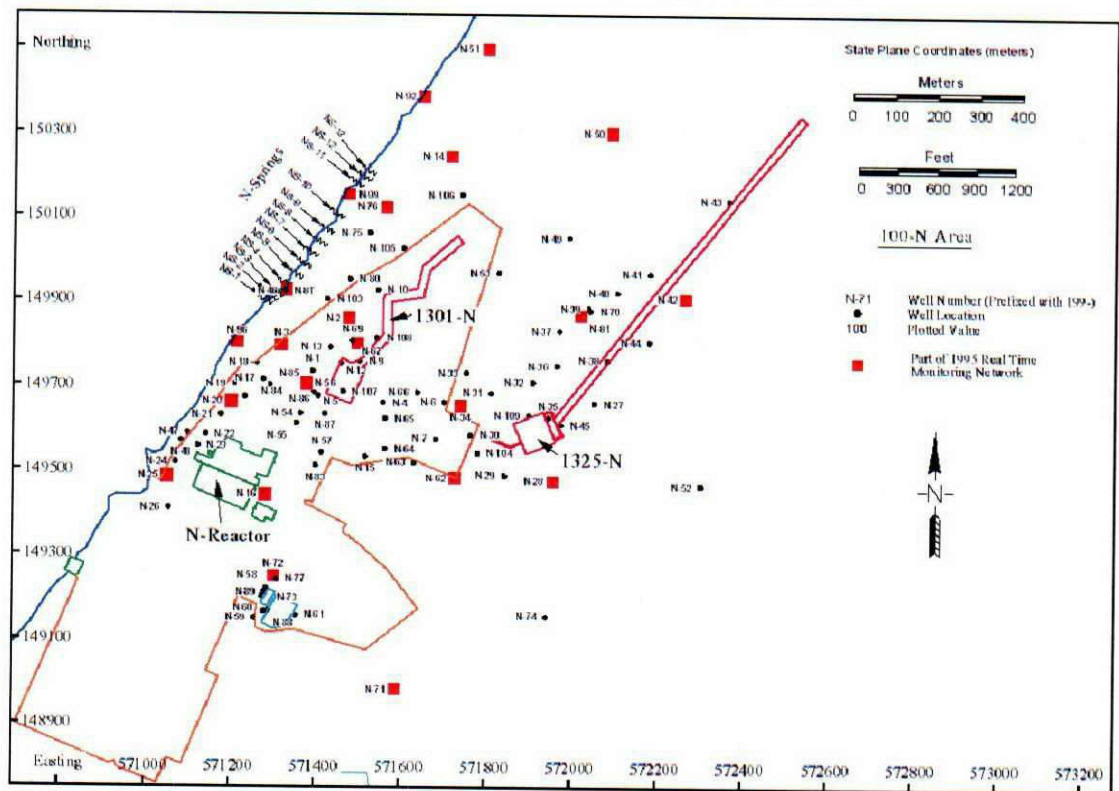


Figure 1-2B. Test Site Location Aerial Photo



1.2 Site Description

1.2.1 Geology

Stratigraphic units of significance in the 100-N Area include the following:

- Elephant Mountain Member of the Columbia River Basalt Group
- Ringold formation
- Hanford formation

The Elephant Mountain Member is an extensive basalt unit that underlies the fluvial-lacustrine deposits of the Ringold formation and glaciofluvial deposits of the Hanford formation. The Ringold formation is composed of several lithologic facies. Of most interest at 100-N is the Ringold Unit E, which forms the unconfined aquifer beneath the Hanford formation, and the Ringold Upper Mud Unit, which forms the base of the unconfined aquifer and is believed to be an aquitard for Unit E.

1.2.2 Hydrogeology

The uppermost stratigraphic unit in the 100-N area is the Hanford formation, which consists of uncemented and clast-supported pebble, cobble, and boulder gravel with minor sand and silt interbeds. The matrix in the gravel is composed mostly of coarse-grained sand, and an open-framework texture is common. For most of the 100-N Area, the Hanford formation extends from ground surface to just above the water table, 5.8 to 24.5 meters (19 to 77 feet) in thickness. However, channels of Hanford gravels extending below the water table occur.

The uppermost Ringold stratum at 100-N is Unit E, consisting of variably cemented pebble to cobble gravel with a fine- to coarse-grained sand matrix. Sand and silt interbeds also may be present. Unit E forms the unconfined aquifer in the 100-N Area and is approximately 12 to 15 meters (39 to 49 feet) thick. The base of the aquifer is situated at the contact between Ringold Unit E and the underlying, much less transmissive, silty strata referred to locally as the Ringold Upper Mud, approximately 60 meters (197 feet) thick.

The Hanford formation is much more transmissive than the underlying Ringold Unit E. However, due to geologic heterogeneity, the hydraulic conductivity in both units is highly variable. Typical values of 15 and 182 m/d have been used for modeling purposes for the Ringold and Hanford units, respectively (Hydrogeologic, Inc., 2001).

Figure 1-3 depicts a cross-section of the Hanford and upper Ringold units in the near-river environment. As illustrated in Figure 1-3, the aquifer outcrops into the Columbia River channel and the high river stage rises into the Hanford formation.

Groundwater flows primarily in a north-northwesterly direction most of the year and discharges to the Columbia River. The groundwater gradient varies from 0.0005 to 0.003 m/m. Near the LWDF facilities, average groundwater velocities are estimated to be between 0.03 and 0.6 m/d (0.1 and 2 ft/d), where 0.3 m/d (1 ft/d) is generally considered as typical. However, groundwater flows near the river are significantly influenced by the Columbia River's seasonal high and low water levels, as shown in regional water table maps

(Figures 1-4A and 1-4B). In June 1995, the water table was relatively flat and the hydraulic gradient was inland, away from the Columbia River in the near-river environment. By October, the water level of the Columbia River dropped, resulting in steeper hydraulic gradients and groundwater flow toward the Columbia River.

1.2.3 Groundwater-River Interaction

Fluctuations in river stage resulting from seasonal variations and daily dam operations have a significant impact on groundwater flow direction, hydraulic gradient, and groundwater levels near the river. The volume of water moving in and out of the unconfined aquifer on both a daily and seasonal basis is an order of magnitude greater than groundwater flowing as a result of the regional hydraulic gradient. In addition, with the changing direction of groundwater flow, pore water velocities near the river may exceed 10 m/d (32.8 ft/d) (Hydrogeologic, 1999). During the high river stage, river water moves into the bank and mixes with groundwater. The zone of mixing is restricted to within tens of meters of the shoreline. During low river stage, this bank storage water drains back into the river and may be observed as springs along the riverbank. Springs, seeps, and subsurface discharge along the Columbia River bank are the primary pathway of 100-N groundwater contaminants to the Columbia River.

Figure 1-3. Site Conceptual Model in Cross-Section

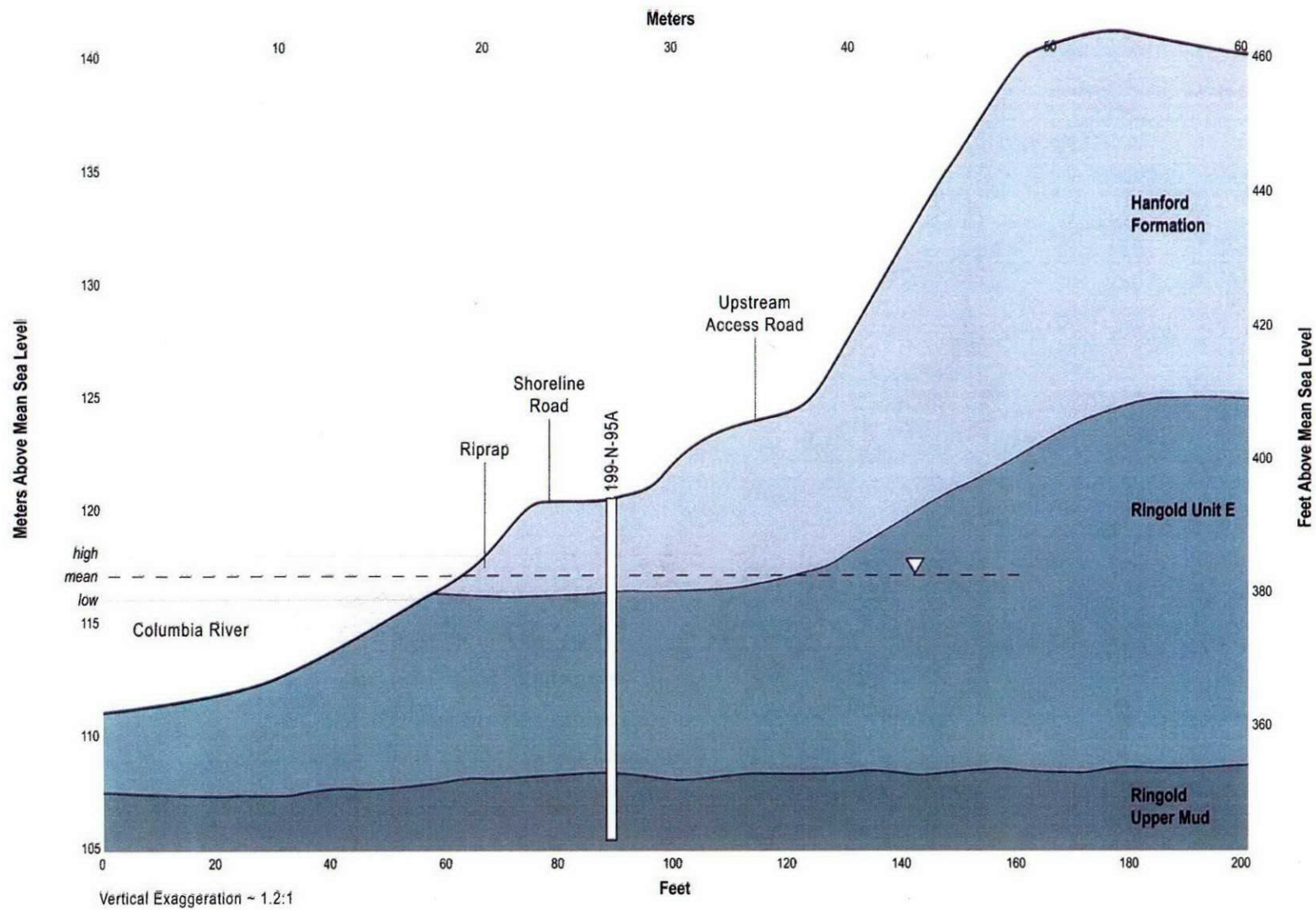


Figure 1-4A. Water Table Elevations: High River Stage

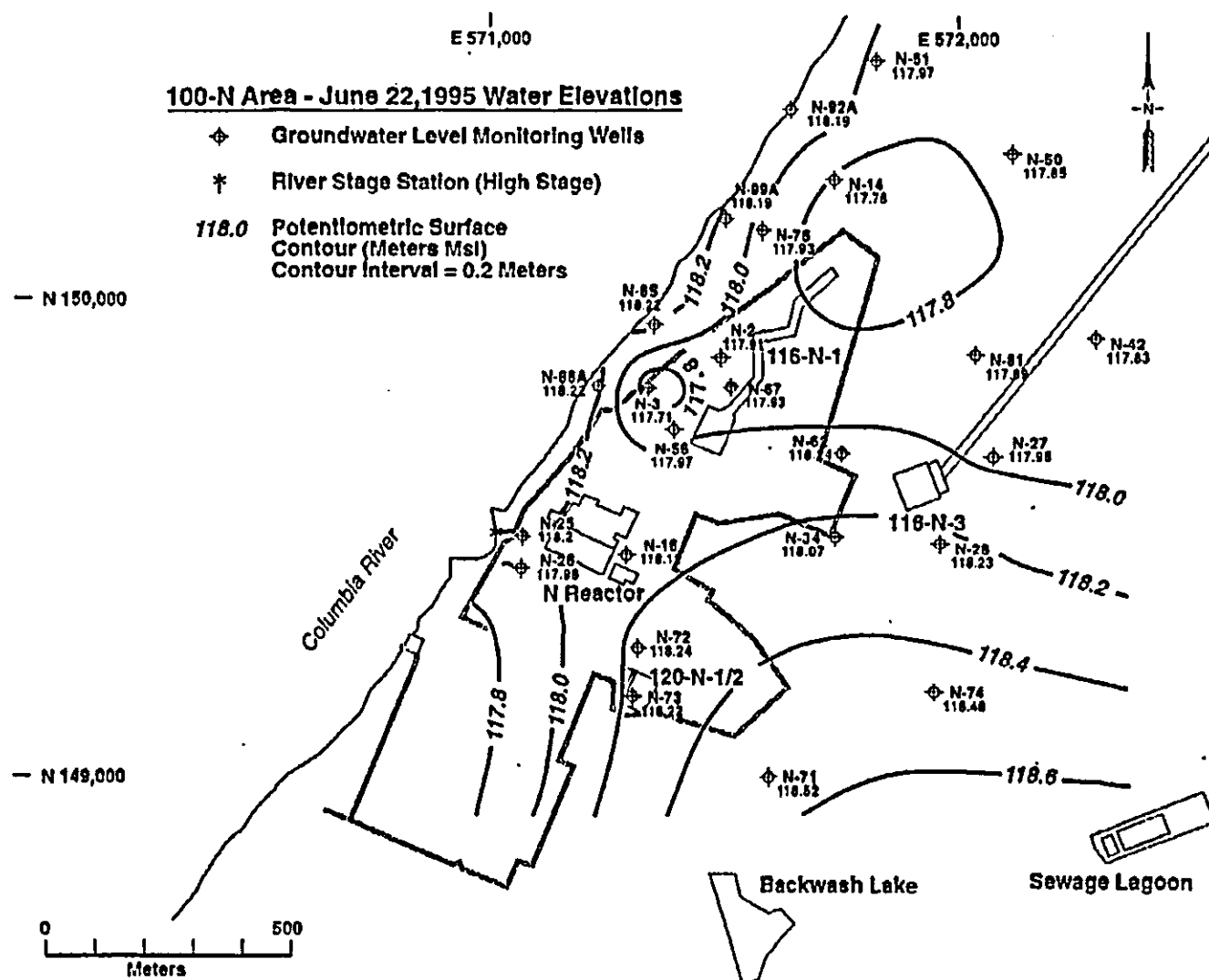
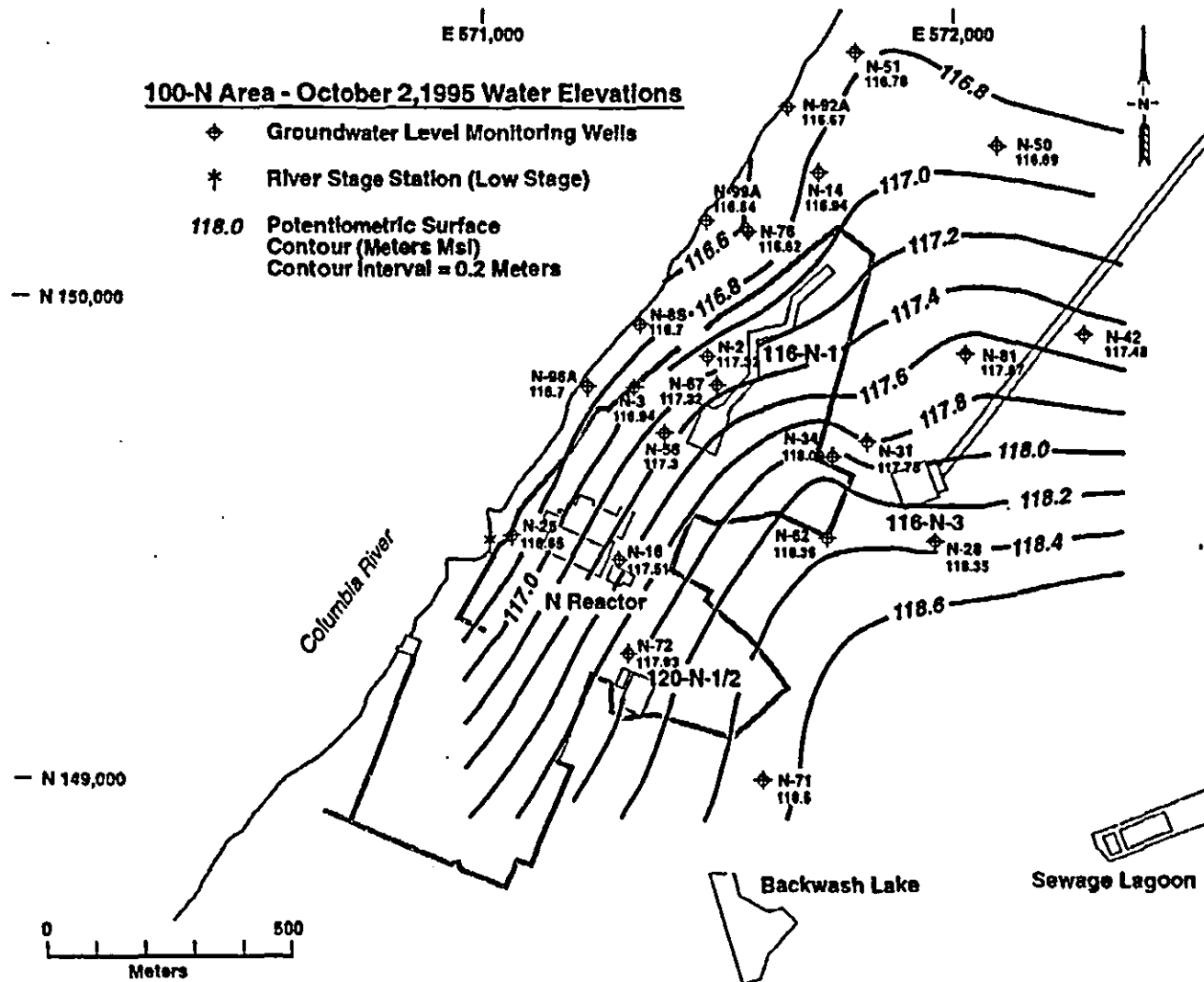


Figure 1-4B. Water Table Elevations: Low River Stage



1.3 Nature and Extent of ^{90}Sr Contamination

Groundwater at 100-N has been contaminated with various radionuclides and non-ionic and ionic constituents. Of primary concern is the presence of ^{90}Sr in the groundwater and the discharge of ^{90}Sr to the Columbia River via groundwater. ^{90}Sr is more mobile than other radiological contaminants found at the site (with the exception of tritium), and because of its chemical similarity to calcium, it bioaccumulates in plants and animals. With a half-life of 28.6 years, it will take approximately 300 years for the ^{90}Sr concentrations present in the subsurface at 100-N to decay to below current drinking water standards.

The zone of ^{90}Sr -contaminated soils resulting from 30 years of wastewater discharge to the LWDFs includes the portions of the vadose zone that were saturated during discharge operations, and the underlying aquifer, which extends out to the Columbia River (Figure 1-5). During operations, a groundwater mound approximately 6 meters (20 feet) high was created. Not only was the water table raised into more transmissive Hanford and Ringold sediments, but steeper hydraulic gradients were created, increasing the groundwater flow rate toward the river. While the 100-N Reactor was operating, riverbank seepage was pronounced. Since that time, the number of springs and seeps has decreased in proportion to the decrease in artificial recharge caused by the wastewater disposal.

The majority of the 1,500 curies (Ci) of ^{90}Sr remaining in the unsaturated and saturated zones in the 100-N Area as of 2003 (DOE-RL, 2004), is present in the vadose zone above the aquifer. An estimated 72 Ci of ^{90}Sr are contained in the saturated zone, and approximately 0.8 Ci are in the groundwater. Data from soil borings collected along the riverbank indicate that ^{90}Sr concentrations in soil reach a maximum near the mean water table elevation and then decrease with depth (BHI, 1995) (see Figure 1-6). Groundwater concentrations reflect the soil concentrations. Because ^{90}Sr has a much greater affinity for sediment than water (high K_d), its rate of transport in groundwater to the river is considerably slower than the actual groundwater flow rate. The relative velocity of ^{90}Sr to groundwater is approximately 1:100. Under current conditions, approximately 0.14 to 0.19 Ci are released to the Columbia River from the 100-N Area annually (TAG, 2001). The expectation for performance of the apatite PRB, and secondary polishing treatment if needed, is to reduce the estimated 0.14 to 0.19 Ci/yr released to the river by > 90 percent. But more importantly, the pore fluid ^{90}Sr concentrations at the shoreline should be significantly reduced by the planned alternative treatment, which in turn will reduce exposure of aquatic biota in the near-shore region where NR-2 groundwater enters the river.

In 1995, the ^{90}Sr groundwater plume extended approximately 400 meters (1,300 feet) along the river's length between the 1,000 picocuries per liter (pCi/L) contours, and approximately 800 m (1,600 feet) between the 8 pCi/L (the drinking water standard) contours (Figure 1-7) (Hydrogeologic, 1999). The highest concentrations along the shoreline were observed between wells N-94 and N-46. An area of "preferential flow" was identified in the *Technical Reevaluation of the N-Springs Barrier Wall* (BHI, 1995), that encompasses N-94, N-95, and N-46. Because of an erosional feature in the Ringold Unit, the Hanford formation dips below the water table at this location, forming a more transmissive flow path between the disposal crib and the Columbia River (Figure 1-8). Wastewater appears to have concentrated along

this route, resulting in higher concentrations in this area than would be predicted based on regional groundwater flow direction (see Figure 1-4B).

Based on recent aquifer tube and clam data (Figure 1-9), most of the ^{90}Sr currently entering the river appears to be limited to a relatively narrow zone (~300 feet) within the hypothesized preferential flow zone. The treatability test for the apatite PRB will concentrate on this zone first. The need for and extent of expansion beyond this zone will be based on risk assessment findings and the administrative process for the final remedy.

N-Springs data from 1985 to 1991 showed significantly higher concentrations of ^{90}Sr in seep wells NS-2, NS-3, and NS-4 compared to the adjacent springs upstream and downstream (Figure 1-10) (BHI, 1995). Well NS-3 and the neighboring monitoring wells N-46 and N-8T have currently and historically shown the highest ^{90}Sr concentrations along the shoreline, with concentrations as high as 15,000 pCi/L ^{90}Sr observed at N-46 (TAG, 2001; DOE-RL, 2004). Recent clam data collected for the ecological risk assessment (ERA) show that the highest concentrations of ^{90}Sr in clams were observed along approximately 90 meters (300 feet) of riverbank that encompasses NS-1, NS-2, NS-3 and NS-4 (see Figure 1-9). The previous N-Springs data, recent aquifer tube data, groundwater data, and clam data (DOE-RL, 2005) all indicate that treating the 300 feet of shoreline near N-46 will address the highest concentration portion, if not the majority, of the near-shore ^{90}Sr contamination. The targeted length of shoreline is approximately between NS-1 and NS-4 (Figure 1-11).

figure 1-5. Conceptualization of Contamination from Liquid Waste

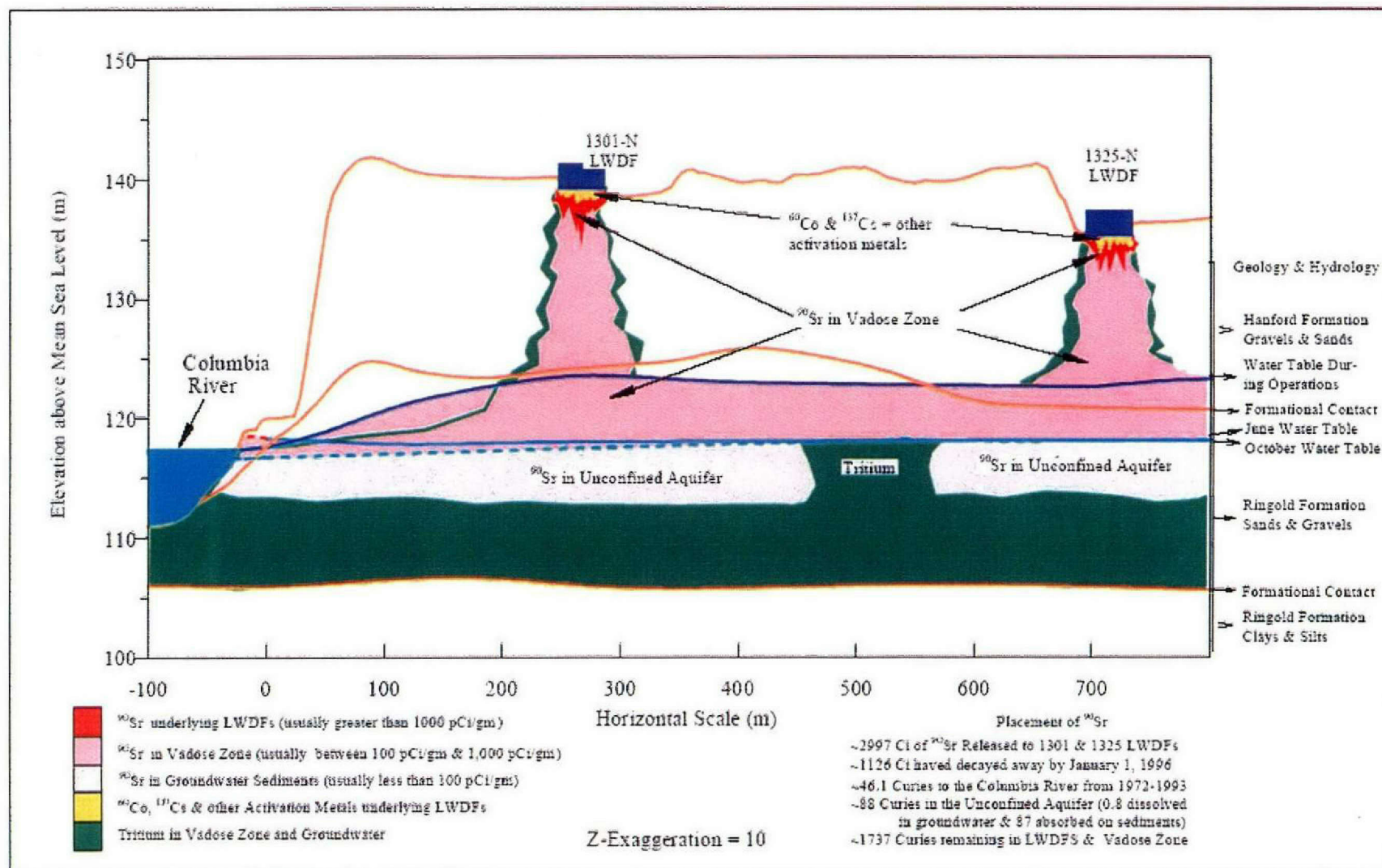


Figure I-6. 100-N Apatite Project, PNNL, Borehole C4473, Well 199-N-121, Geochemical Profile Results

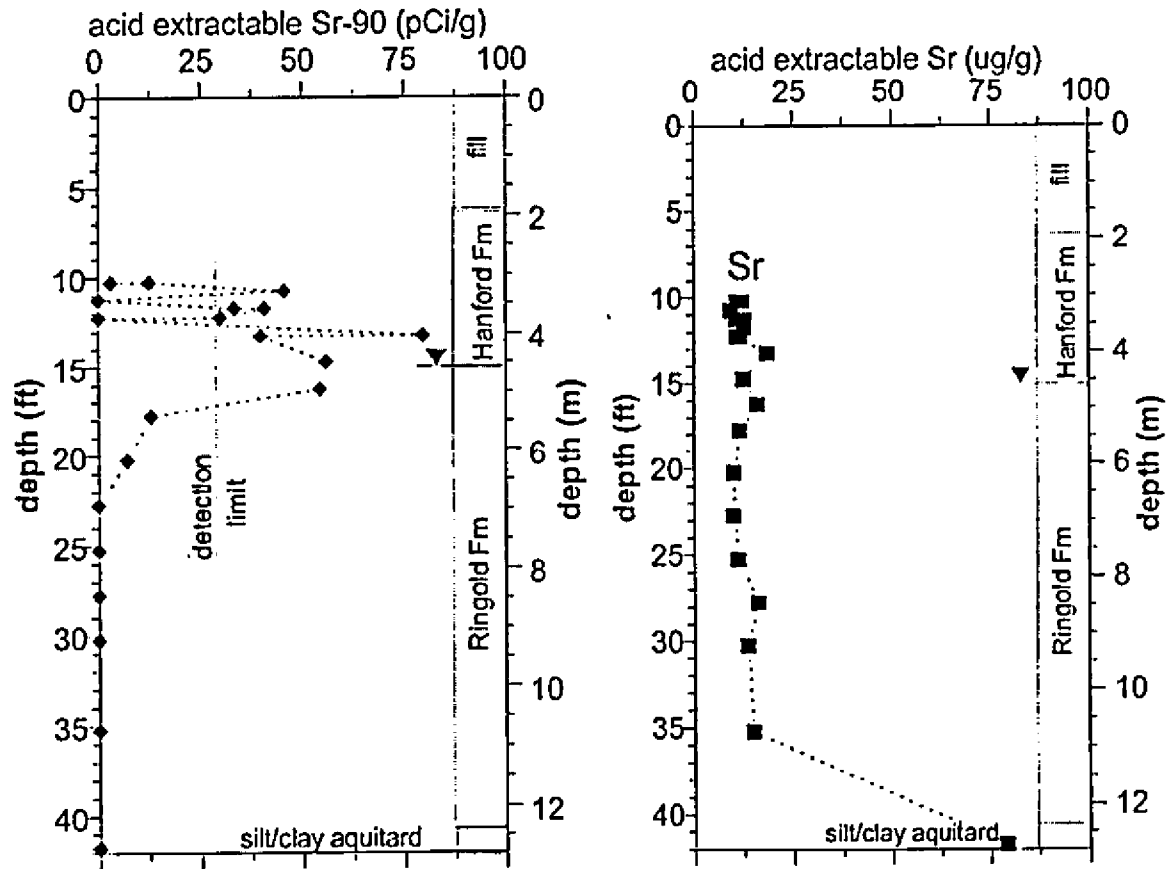


Figure 1-7. 100-N Area ^{90}Sr Concentrations in the Unconfined Aquifer for 1999

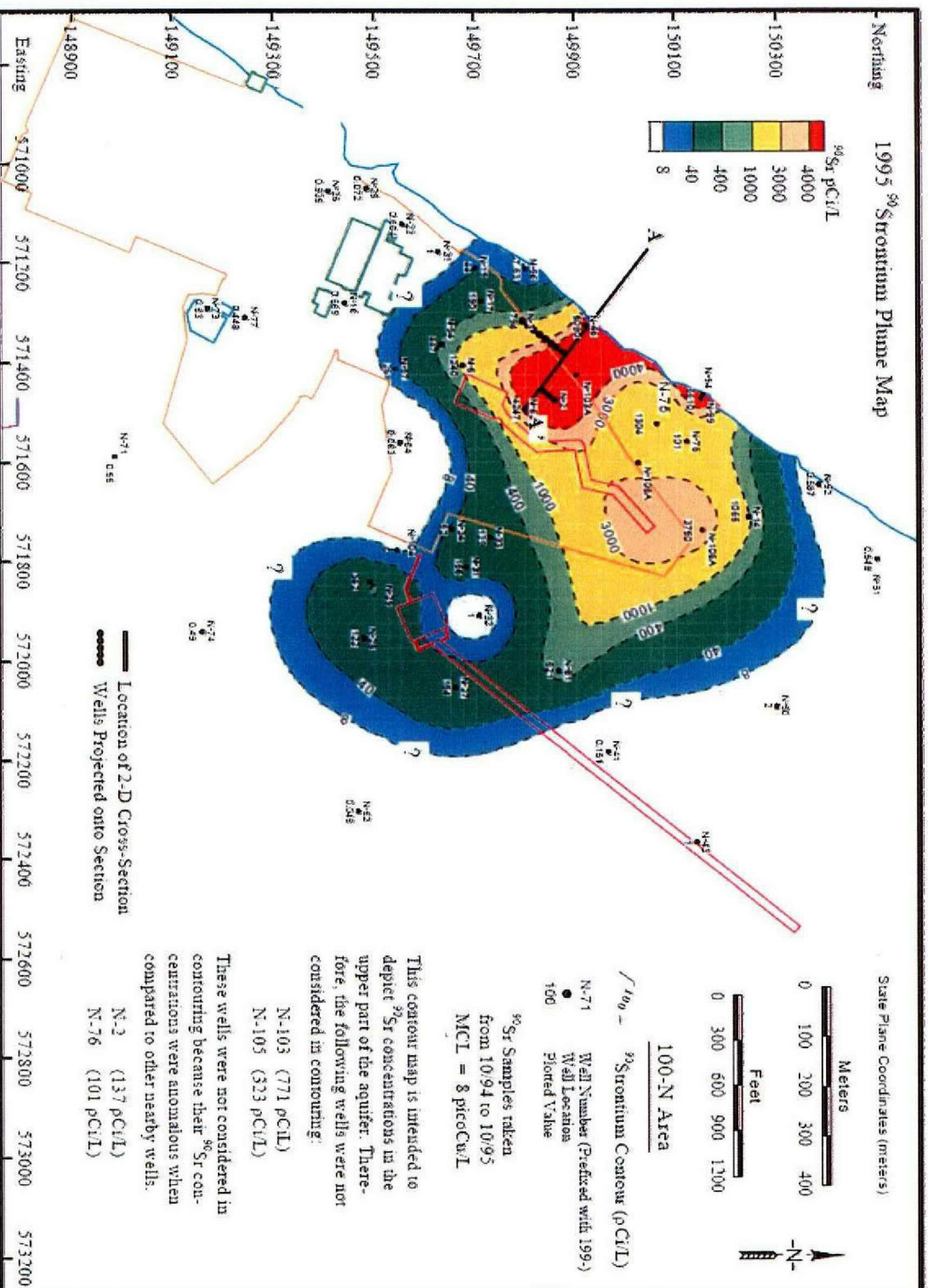


Figure 1-8. ⁹⁰Sr Concentrations in Cuttings Taken from the Groundwater Monitoring Wells and Geotechnical Borings

⁹⁰Strontium Concentrations in Sediments Taken from the New Groundwater Monitoring Wells & Geotechnical Borings

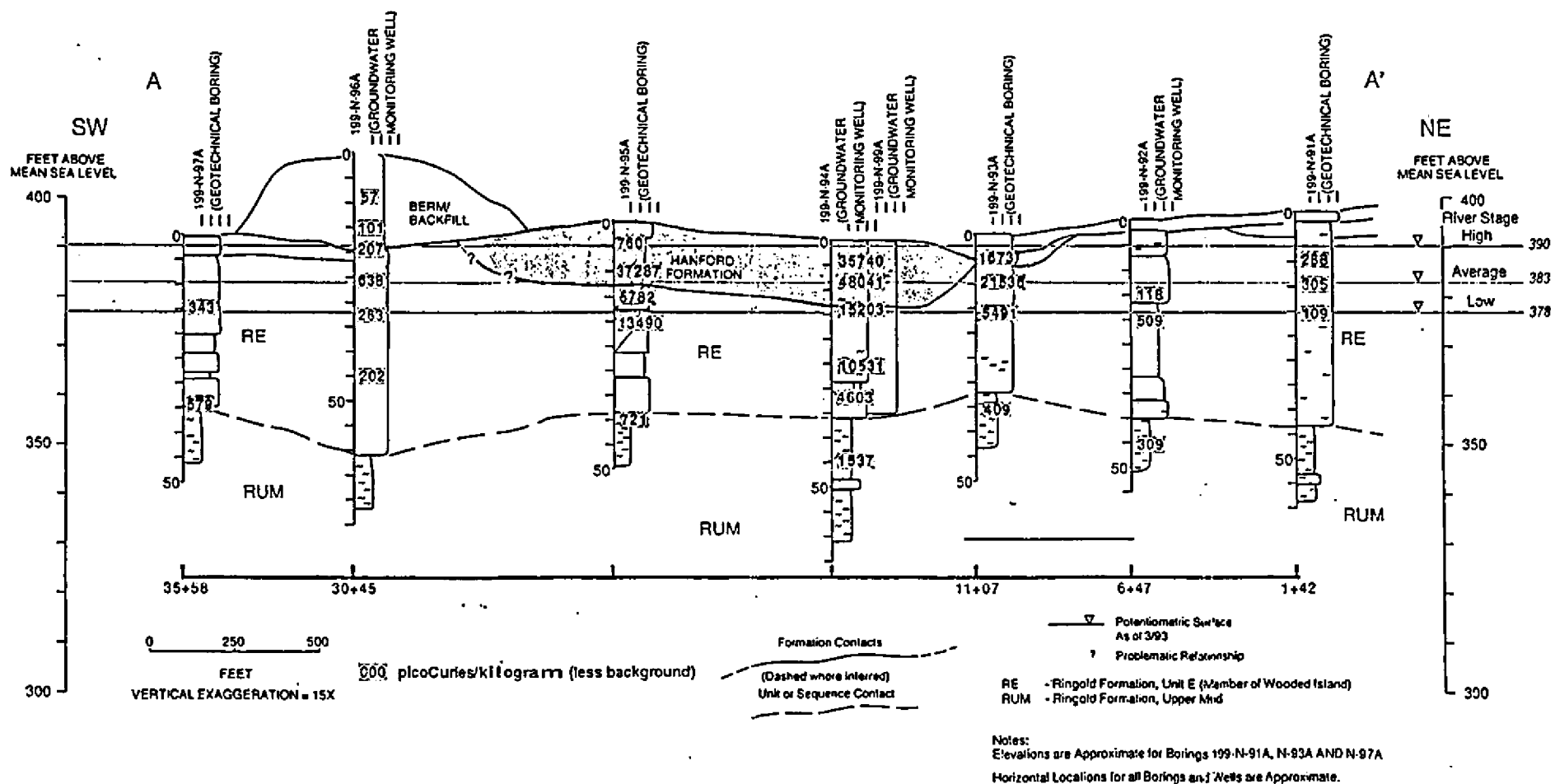


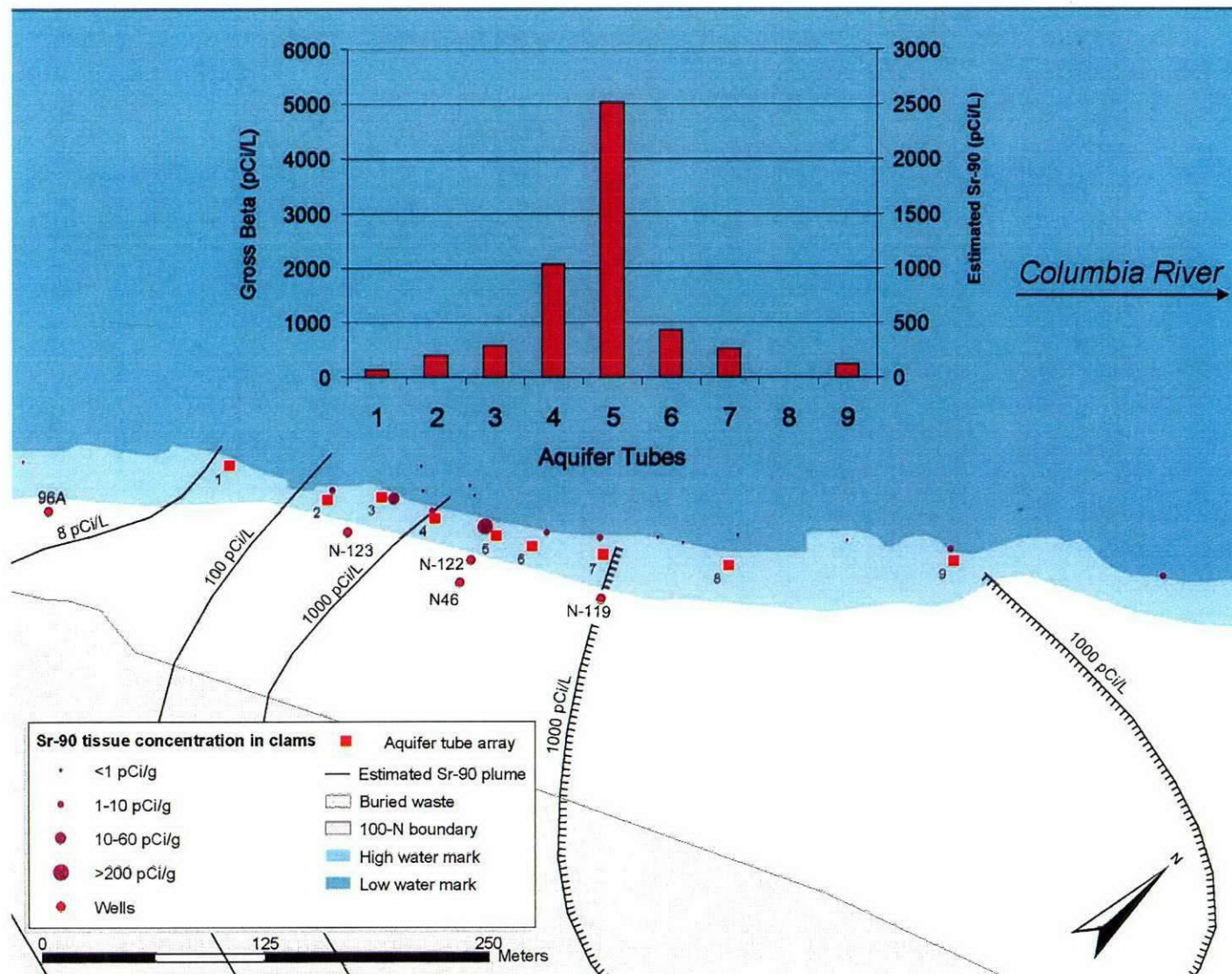
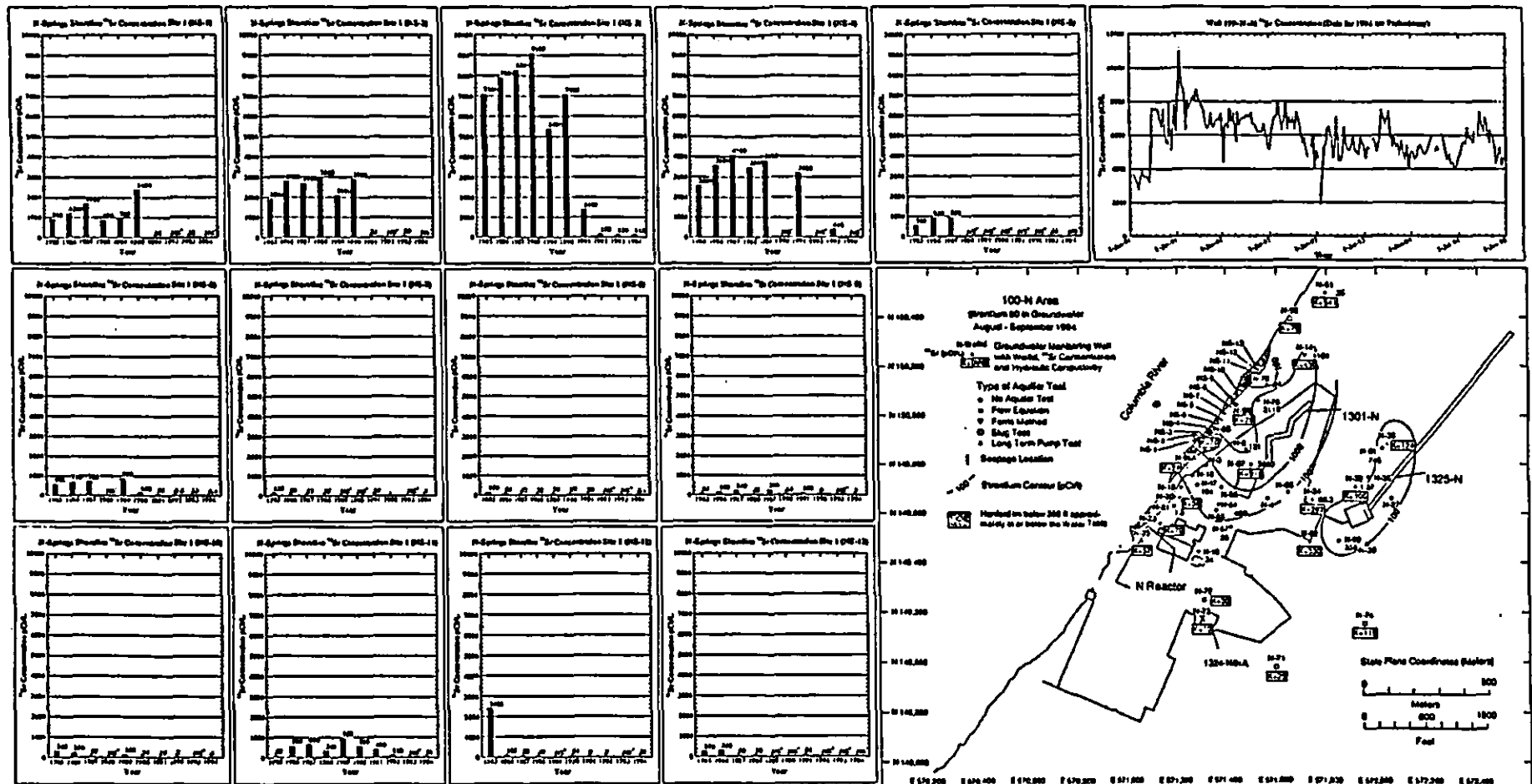
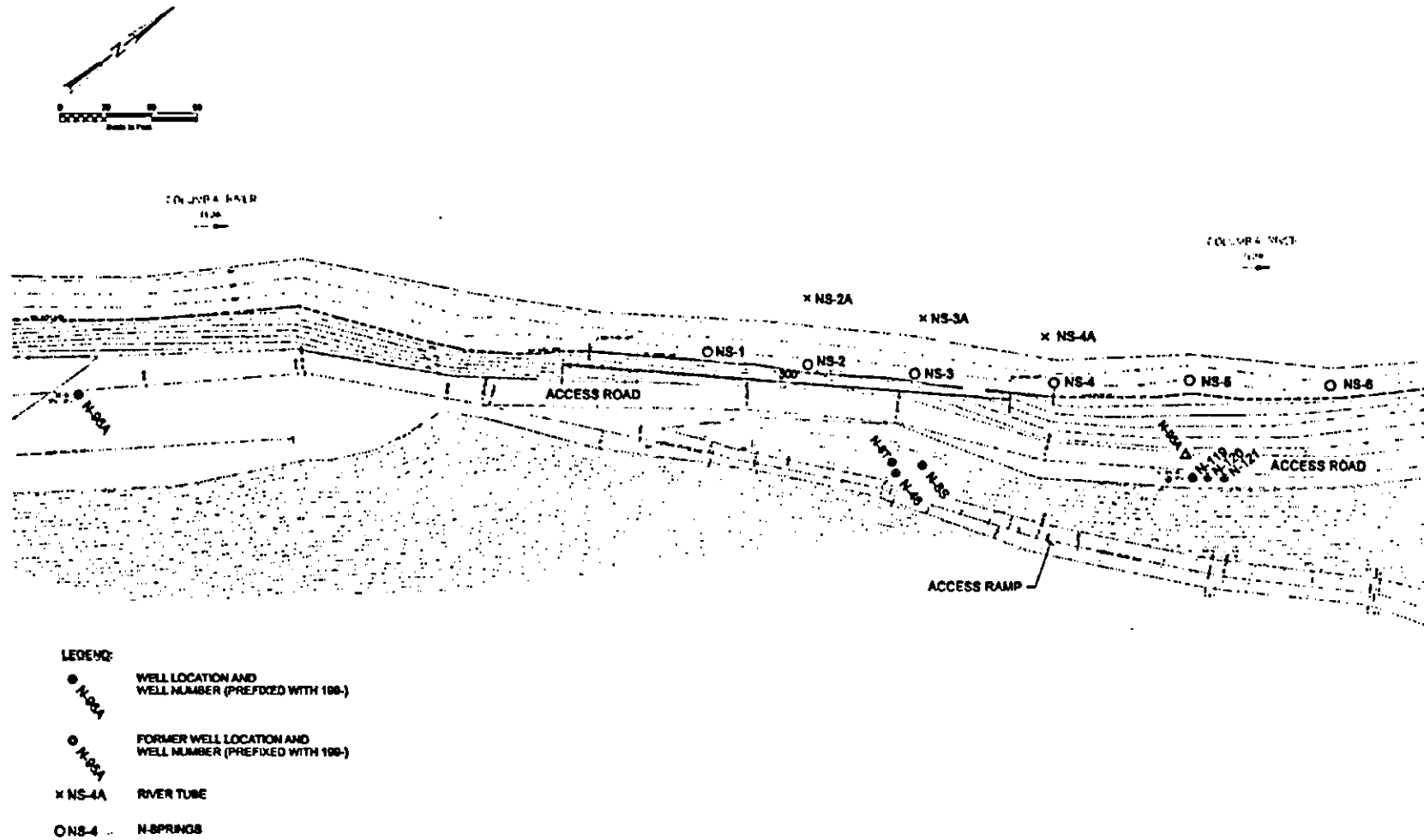
Figure 1-9. ^{90}Sr Concentrations in Clams and Shallow Groundwater (from DOE-RL, 2005)

Figure 1-10. Time History of Contaminants Entering the River at N-Spring



*NS = Not Sampled. For all years except 1993, the seep well was not sample because it went dry. For 1993, the Columbia River Stage was too high and the seep well was not sampled because it was under water. (Person of Communication from Craig Perkins (WHC) to M. P. Connolly on 24-Feb-1994)

Figure 1-11. 100-N Area Treatability Test Plan Site Map



1.4 Remediation History

1.4.1 National Priorities List/Corrective Measures Study

The 100 Areas Superfund Site, which included the 100-N Area and all other reactor sites, was placed on the National Priorities List (NPL) in 1989. This was the same year the Tri-Party Agreement signed by the DOE, U.S. Environmental Protection Agency (EPA), and Ecology established the procedural framework and schedule for the remedial response actions at Hanford. In 1994, the *Limited Field Investigation Report for the 100-NR-2 Operable Unit* (LFI) (DOE-RL, 1994) was published and, based on the data presented, a qualitative risk assessment (QRA) was conducted. The QRA indicated that groundwater contaminants in the 100-NR-2 OU exceeded human health risk levels, prompting an Expedited Response Action to address ^{90}Sr in groundwater. In 1995, a pump-and-treat system was installed as an interim measure to control the movement of ^{90}Sr to the Columbia River.

A corrective measures study (CMS) (DOE-RL, 1997), conducted to support the selection of remedial alternatives to address contamination at the 100-NR-1 and 100-NR-2 OUs, determined that sufficient information was not available to decide a final groundwater remedy. Four alternatives were proposed for consideration as interim remedies (No Action, Institutional Controls, Hydraulic Controls, and Pump-and-Treat), and pump-and-treat was retained as the selected interim remedy because it provides a hydraulic barrier while removing approximately 90 percent of ^{90}Sr from extracted groundwater, and does not preclude any potential final remedies.

The results from the CMS and the Tri-Parties' preference for interim remedial action were summarized in a *Proposed Plan* (DOE-RL, 1998) that was made available to the public in March 1998. In September 1999, the Interim Action Record of Decision (ROD) (Ecology, 1999) was signed by DOE, Ecology, and EPA.

1.4.2 Interim Action Record of Decision

The remedial action objectives (RAOs) for the 100-NR-2 OU were specified on page 35 of the Interim Action ROD:

- Protect the Columbia River from adverse impacts from the 100-NR-2 groundwater so that designated beneficial uses of the Columbia River are maintained. Protect associated potential human and ecological receptors using the river from exposure to radioactive and non-radioactive contaminants present in the unconfined aquifer. Protection will be achieved by limiting exposure pathways, reducing or removing contaminant sources, controlling groundwater movement, or reducing concentrations of contaminants in the unconfined aquifer.
- Protect the unconfined aquifer by implementing remedial actions that reduce concentrations of radioactive and non-radioactive contaminants present in the unconfined aquifer.
- Obtain information to evaluate technologies for ^{90}Sr removal and evaluate ecological receptor impacts from contaminated groundwater (by October 2005, as amended).

- Prevent destruction of sensitive wildlife habitat. Minimize the disruption of cultural resources and wildlife habitat in general and prevent adverse impacts to cultural resources and threatened or endangered species.

The major components of the selected remedy for the 100-NR-2 groundwater OU as stated in the Interim Action ROD (page 52) include:

- Remove ⁹⁰Sr-contaminated groundwater through extraction and treatment with ion exchange and discharge treated groundwater upgradient into the aquifer.
- Maintain Ecology-approved groundwater monitoring well networks to monitor pump-and-treat operations and impacts to groundwater.
- Evaluate technologies for ⁹⁰Sr removal and submit information to Ecology by October 2004.
- Evaluate aquatic and riparian receptor impacts from contaminated groundwater and submit information to Ecology by October 2005 (an amendment changed the original October 2004 date to allow closer coordination with the river corridor risk assessment).

The Interim Action ROD requires that "DOE will investigate groundwater remediation and river protection technologies for ⁹⁰Sr contamination and submit information to Ecology within 5 years of this ROD." "...Pump-and-treat may be considered as an integral part of other alternatives; however, groundwater remediation technologies to be evaluated will focus on innovative technologies to remove ⁹⁰Sr from contaminated sediments and groundwater." (Page 53.)

To fulfill the requirements of the Interim Action ROD:

- The pump-and-treat system has operated continuously since 1995. Groundwater monitoring has been conducted as approved by Ecology, and annual reports summarizing the monitoring data and pump-and-treat system have been submitted each year since the beginning of operations in 1995.
- Under the Innovative Treatment and Remediation Demonstration (ITRD) Program, the Technical Advisory Group (TAG) for the 100-N Area completed the *Hanford 100-N Area Remediation Options Evaluation Summary Report* in November 2001 (TAG, 2001).
- *Strontium-90 at the Hanford Site and its Ecological Implications* (PNNL) was submitted to DOE in May 2000.
- An ERA is underway in accordance with an approved sampling and analysis plan (DOE-RL, 2005). A comment draft report was submitted to Ecology on October 31, 2005.
- A letter report, *Evaluation of Strontium-90 Treatment Technologies for the 100-NR-2 Groundwater Operable Unit*, was submitted to DOE in October 2004 by Fluor/CH2M HILL (Fluor/CH2M HILL, 2004). This letter report and related public workshop comments (December 2004), together with the ITRD Report, completes the technology evaluation requirement specified in the Interim Action ROD. This Treatability Test Plan (TTP) initiates implementation of the previous evaluation efforts.

1.4.3 Pump-and-treat Performance

Installed in 1995, the pump-and-treat system at the 100-N Area uses four extraction wells, a treatment plant, and two injection wells. The pump-and-treat system was intended to reduce the flow of contaminated groundwater toward the Columbia River, and in the process remove some ^{90}Sr from the aquifer.

As described in the Interim Action ROD, insufficient information existed to recommend a final remedy for ^{90}Sr in the 100-NR-2 groundwater. Therefore, Ecology, EPA, and DOE proposed to control movement of ^{90}Sr to the Columbia River as an interim remedial action for river protection. This control was to be provided by the existing pump-and-treat system. The apparent length of near-shore region influenced or "controlled" by the capture zone of the pump-and-treat system is approximately 1,300 feet (400 meters; Figure 1-12).

At a pumping rate of 60 gallons per minute (gpm), the pump-and-treat system extracts approximately 0.2-Ci/year, which is about 10 times less than the amount removed by radioactive decay of the ^{90}Sr stored in the aquifer (DOE-RL, 2004). As of June 2004, 1.6 Ci of ^{90}Sr have been removed since beginning operations in 1995. Given that there is approximately 80 Ci of ^{90}Sr in the saturated sediments in the 100-N Area, at this removal rate the time needed to meet the drinking water standard (8 pCi/L) is approximately 270 years.

Despite the hydraulic containment provided by the pump-and-treat system, elevated ^{90}Sr concentrations near the shoreline have persisted since the beginning of pump-and-treat operations. Figure 1-13 illustrates the impact of the pump-and-treat system on ^{90}Sr concentrations in the groundwater at the riverbank. The green line shows that discharge to the cribs discontinued in 1991. The red line shows annual average concentrations of ^{90}Sr in porewater at well N-46, which is located at the road along the riverbank within the ^{90}Sr plume. Concentrations steadily increased from 1980 until about 1989. Since that time, concentrations have fluctuated widely, presumably in response to river stage and sampling date relative to water level. Nevertheless, near-shore pore fluid ^{90}Sr concentrations have remained elevated. This observation confirms modeling results indicating that ^{90}Sr in the near-shore aquifer or stream bank storage zone will decline primarily by radioactive decay. In marked contrast, tritium (a non-adsorbing, 100-NR-2 co-contaminant) declined rapidly after the beginning of pump and treat operations and is currently at or below the detection limit (~200 pCi/L) in near-shore groundwater samples, but remains elevated (average of about 20,000 pCi/L) in the pump and treat capture zone (Calendar Year 2005 Summary of 100-Area Pump and Treat Operations, DOE-RL 2006-08). This observation provides evidence that the predicted hydraulic containment functioned as designed.

Although the pump-and-treat system may have met the objective of reducing the flow of groundwater (and non-adsorbing co-contaminants) in the strontium-90 plume area to the river, it has not met the objective of reducing strontium-90 concentrations in aquifer pore fluid at the shoreline or in the stream bank storage zone. Minimizing exposure of eco-receptors in the near-shore aquatic and riparian zone to strontium-90, the primary 100-NR-2 contaminant of potential ecological concern (DOE-RL 2005), requires a different approach.

Figure 1-12. 100-NR-2 Pump-and-Treat System

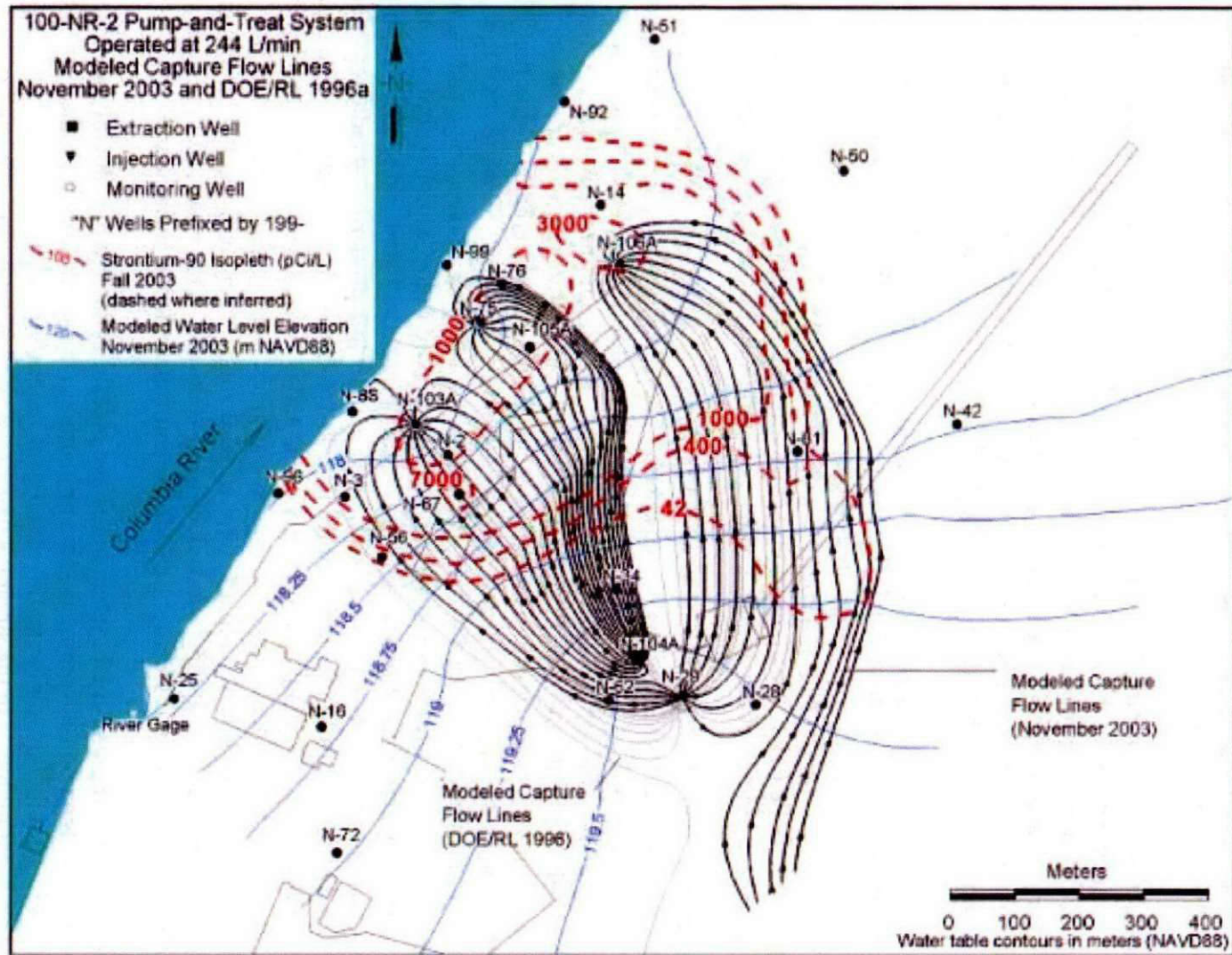
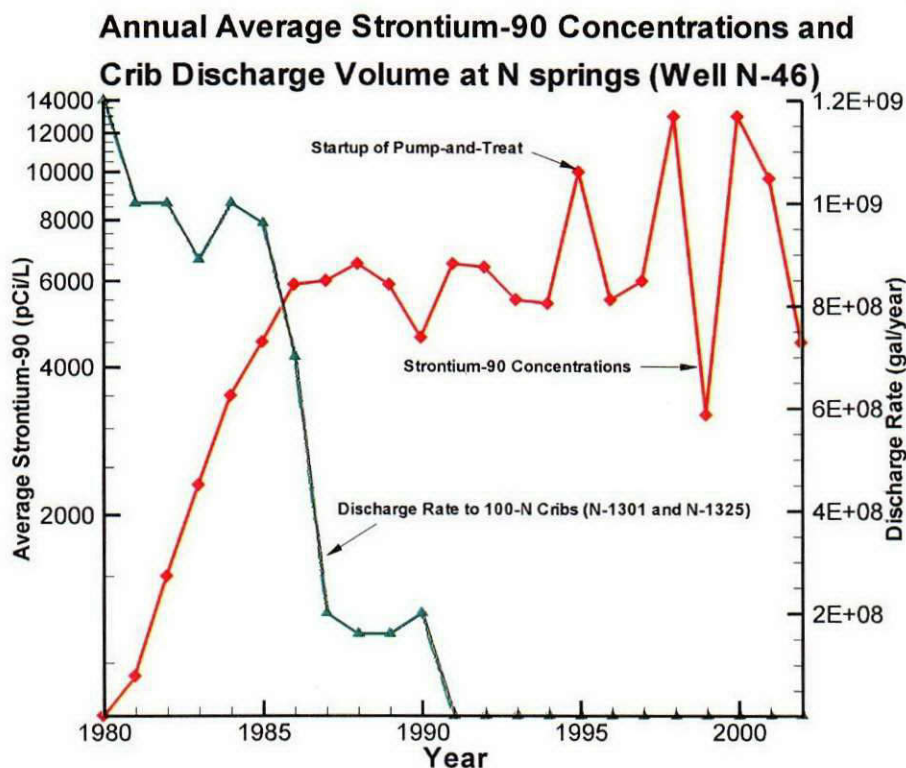


Figure 1-13. ^{90}Sr Concentrations in Groundwater at 100-N

History of annual wastewater discharge to the soil column and strontium-90 concentrations in groundwater near the shoreline at n-springs (well n-46.) The wide fluctuations that occur in the 1995 to 2000 period are attributed to unusually high (and low) annual average river stages during that time period. The unusually high water mobilized ^{90}Sr stored above the mean water table, causing higher average concentrations in groundwater. The correlation between water level and concentration has been observed in other nearby monitoring wells (for example, n-67).

1.4.4 ITRD Report

In the ITRD Report, the TAG considered various technologies that would meet the RAOs identified in the Interim Action ROD for protecting the river and the unconfined aquifer, and retained five technologies for further evaluation. TAG's conclusions and recommendations for each technology are presented in Table 1-1.

Table 1-1. ITRD Technology Evaluation

Technology	Conclusion	Recommendation
Monitored Natural Attenuation (MNA)	May be appropriate for portion of plume far from the river, but will not limit current discharges of ^{90}Sr from N-Springs.	Should be examined in more detail when establishing Long-Term Stewardship protocols.
Soil Flushing	Likely to be effective in removing ^{90}Sr in the shortest time frame.	Should be examined in more detail with regulators.
Phytoremediation	May be the best option for controlling current releases at the river; leaf litter control may be an issue.	Needs more analysis.
^{90}Sr stabilization by phosphate injection	Design studies were insufficient to support recommendation of the option.	Re-examine this option after the Tanks Focus Area work is completed.
Barrier technologies (clinoptilolite and sheet pile/cryogenic)	Installation is considered feasible. Bank is stable and erosion potential associated with construction is considered negligible.	Precautions during construction should minimize potential damage.

Based on this evaluation, the ITRD concluded that the DOE should evaluate the following remediation scenarios in more detail:

- Monitored Natural Attenuation (MNA)
- Clinoptilolite Barrier with MNA
- Clinoptilolite Barrier with Phytoremediation on the river side of the barrier
- Sheet Pile/Cryogenic Impermeable Barrier with MNA
- Sheet Pile/Cryogenic Impermeable Barrier with Phytoremediation on the river side of the barrier and Soil Flushing on the inland side

Several important developments occurred prior to and since the completion of the ITRD Report:

- Installation of a sheet pile wall was attempted and found not feasible at this particular site.
- The TAG determined that soil flushing was infeasible, primarily because of the massive volumes of lixiviant required for injection and removal, and the problems inherent in treating and disposing large volumes of radioactive wastewater.

- Renewed interest in ^{90}Sr stabilization by phosphate injection (aqueous injection) is based on reports of successful bench testing at Sandia National Laboratory (SNL).

The merits of apatite sequestration and phytoremediation were presented at a workshop in August 2003 by PNNL and SNL scientists. Because of the potential for these technologies to remove or sequester ^{90}Sr from the near-river sediments, DOE funded two laboratory studies at PNNL in FY04 to determine their appropriateness for the 100-NR-2 OU:

- Phytoremediation of ^{90}Sr
- ^{90}Sr Sequestration by Apatite

1.5 Evaluation of ^{90}Sr Treatment Technologies

1.5.1 Letter Report

Submitted to DOE in October 2004, the Letter Report evaluated the most promising treatment alternatives and proposed a path forward for selecting and testing alternatives (Fluor/CH2M HILL 2004). Alternatives evaluated included permeable reactive barriers (PRBs), impermeable barriers, MNA, and phytoremediation. At that time, the final length of the barrier walls was assumed to be about 2,000 feet (600 meters).

Four PRB technologies were considered: vertical hydro-fracture, aqueous injection, air injection, and trenching. These technologies, with the exception of aqueous injection, emplace some form of mineral apatite into the subsurface to sequester ^{90}Sr . In aqueous injection, apatite precursors are introduced as dissolved chemicals into the aquifer via injection wells, and apatite precipitates in a treatment zone surrounding (and downgradient of) the point of injection.

Impermeable barriers reduce ^{90}Sr entering the river by increasing the groundwater flow path around the 2,000 foot barrier to allow time for the ^{90}Sr to decay. Alternatives included a slurry wall via trenching, and a bentonite grout curtain installed via hydro-fracture. MNA allows for the natural decrease of ^{90}Sr concentrations over time, and phytoremediation uses plants to extract ^{90}Sr from the root zone on the riverbank.

One of the outcomes of the technology screening presented in the Letter Report was the decision that barrier walls constructed via trenching are not feasible along the shoreline. The letter report also reiterated the conclusion from the ITRD (2001) that MNA may be appropriate for portions of the plume far from the river, but will not limit current discharges of ^{90}Sr to the river. Phytoremediation was retained for consideration in conjunction with a barrier, but is not regarded as a stand-alone solution for the near-shore area.

The remaining technologies (aqueous injection PRB, air injection PRB, hydrofracture PRB, and hydrofracture grout curtain) were evaluated based on effectiveness, implementability, reduction of near-shore contamination, public acceptance, risk, and cost (Fluor/CH2M HILL 2004). Overall, these technologies compared closely, and the evaluation did not point clearly to a single approach. However, because aqueous injection has the potential to treat the

sediments at the shoreline, the Letter Report recommended that it be the first technology to test in the field.

1.5.2 Post-Letter Report

Presentation of the Letter Report to the public in December 2004 prompted considerable debate about which technology to field test in 2006. Laboratory testing of the feasibility of ^{90}Sr sequestration by aqueous injection continued throughout 2004 and into 2005 at PNNL. In addition, column studies were conducted in 2005 at the Applied Sciences Laboratory (CH2M HILL) to determine which type of commercially available apatite would be the best choice for ^{90}Sr removal by air injection or hydrofracture PRBs, assuming that one or both of these technologies may be implemented in the future.

Based on results from recent investigations presented in Section 1.3, a decision was made to focus on the section of shoreline with the highest ^{90}Sr concentrations for a treatability test. Additionally, it was understood that even if contaminated groundwater from upgradient sources is intercepted, ^{90}Sr impacts on the near-shore aquatic and riparian zone of the Columbia River will continue until contaminants in the riverbank sediments, as well as in the vadose zone, at the near shore have been removed or stabilized. With this change in focus, the apatite sequestration technologies were reevaluated primarily on the basis of which media they target:

- Vertical hydrofracture PRB and vertical hydrofracture impermeable barrier will treat groundwater upgradient of the barrier only
- Air injection PRB will treat upgradient groundwater, and has potential to treat some of the near-shore aquifer
- Aqueous injection PRB will treat upgradient groundwater, the near-shore aquifer, and may also be used to treat the vadose zone

None of these technologies has been tested in the field at Hanford, and there is considerable uncertainty regarding the long-term success of each. However, because it is the only technology that has the potential to reach all of the target areas, the first field trials will assess aqueous injection. While the focus of this TTP will be on aqueous injection, the other technologies are potential alternatives for future testing if aqueous injection is unsuccessful. Vertical hydrofracture and air injection PRBs are addressed briefly in Section 2, and results from the apatite bench-scale testing will be presented in a separate addendum.

1.6 Path Forward

As stated in Section 1.4, the pump-and-treat system has not met the objective of reducing ^{90}Sr concentrations in aquifer pore fluid at the shoreline or riverbank storage zone. Evaluation of existing and new near-shore groundwater, aquifer tube data, and biological data collected during 2004 and 2005 indicates persistent and elevated ^{90}Sr contamination in certain sections of the near-shore zone, particularly 300 feet of shoreline near well N-46. These findings have created a sense of urgency to replace the pump-and-treat system with a more effective treatment technology.

The immediate goal, consistent with the interim ROD, has shifted from evaluating various technologies to conducting a treatability test at the near shore using the technology that has the greatest potential to reduce ^{90}Sr concentrations in the vadose zone and the near-shore aquifer where elevated ^{90}Sr concentrations occur in aquatic biota (i.e., ^{90}Sr sequestration by the injection and dispersal of apatite-forming chemical solutions).

If, as a result of this remedy, the ^{90}Sr concentrations reaching the river are reduced cost-effectively, this technology would serve as the primary component of the NR-2 treatment train. As a secondary or polishing step, phytoremediation to enhance treatment of the zone from the river to the apatite sequestration zone may be revisited at a later time depending on the outcome of the aqueous injection test and evaluation of relative risk to aquatic biota in this zone. If this method cannot emplace enough apatite to sequester the estimated amount of ^{90}Sr carried toward the river over the next few hundred years, or if there are unacceptable chemical impacts, then either air injection or vertical hydrofracture could be attempted as a backup to build up the mass of apatite.

1.7 Final Remedy Considerations

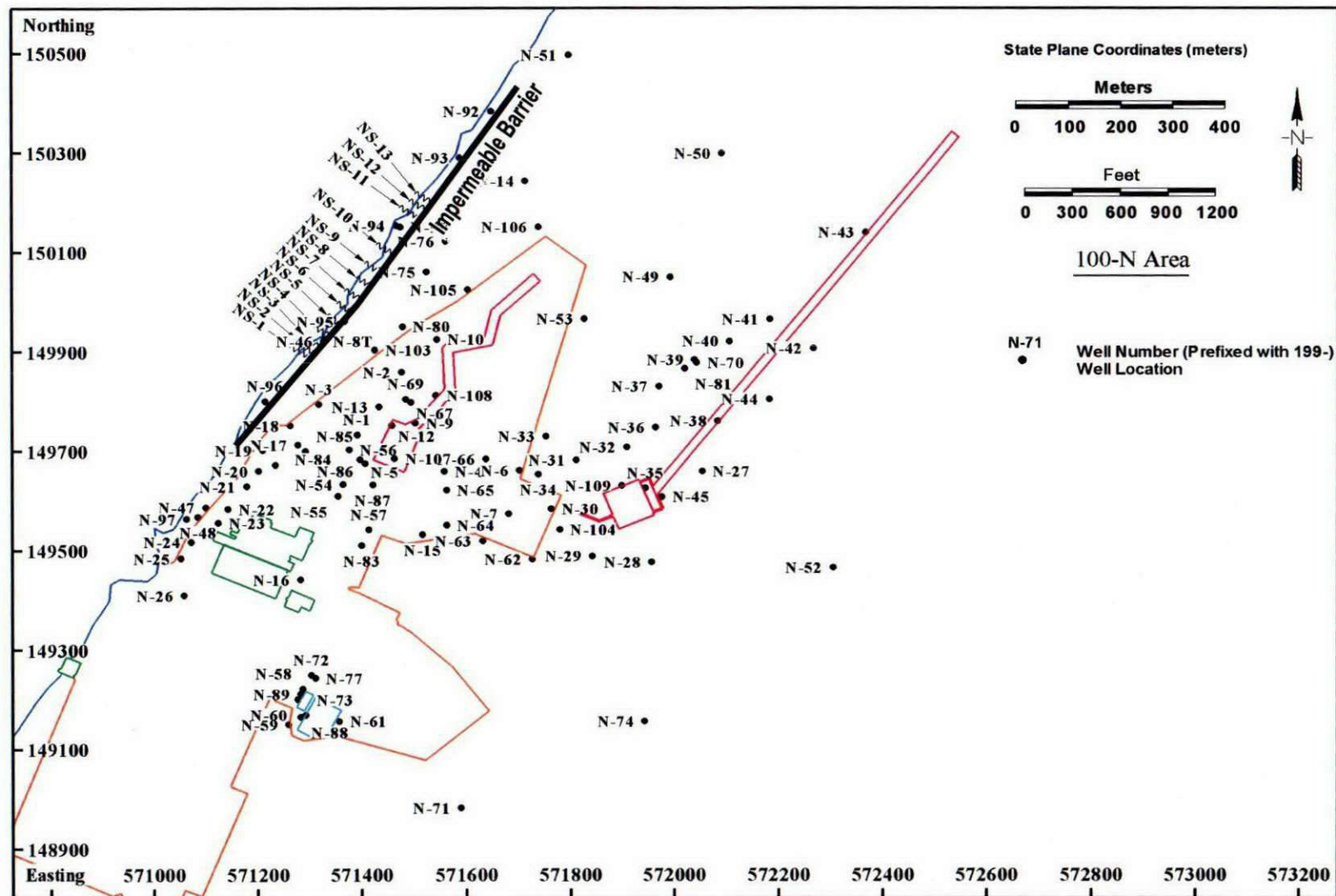
In addition to near-term treatment of the highest near-shore ^{90}Sr concentrations, results of the treatability testing can be used in designing the final remedy after completion of the 100-NR-1/NR-2 risk assessment.

If testing shows that aqueous injection can be used to treat the near-shore aquifer, then appropriate CERCLA administrative actions will be taken to incorporate the treatment into the final remedy. If successful, and depending on the ecorisk assessment findings, this approach could be extended to greater distances along the shoreline.

If aqueous injection does not perform as expected, then installation of an apatite PRB vertical wall via hydrofracture could be attempted, as previously indicated. Phytoremediation and dredging or excavation are potential alternatives that could be used in concert with the hydrofracture wall to address the shoreline. Dredging has not been evaluated but would require some type of coffer dam to contain the slurry of contaminated sediment produced during the dredging operation. Phytoremediation would require a long-term commitment to harvesting the willows and potential containment to prevent offsite transport of contaminated plant tissue.

If neither the aqueous injection nor the hydrofracture apatite PRBs provide adequate results, then an impermeable barrier could be considered to address contaminated groundwater beneath the 100-N Area. A trenchless impermeable wall could be installed parallel to the shoreline (2,000 to 3,000 feet [600 to 900 meters], see Figure 1-14) that would divert any ^{90}Sr upgradient of the wall that enters the groundwater along the wall in either the upstream or downstream direction. The ^{90}Sr would decay during the extended migration path prior to entering the river. This concept was demonstrated previously (BHI, 1995). If a continuous impermeable wall were chosen for the final remedy, it would be necessary to sacrifice the 300-foot PRB section. However, installation of a 300-foot PRB in FY06 would not preclude potential application of a continuous impermeable wall as part of an NR-1/NR-2 final remedy.

Figure 1-14. Conceptual Illustration of Final Remedy as a 3,000-foot Impermeable Barrier

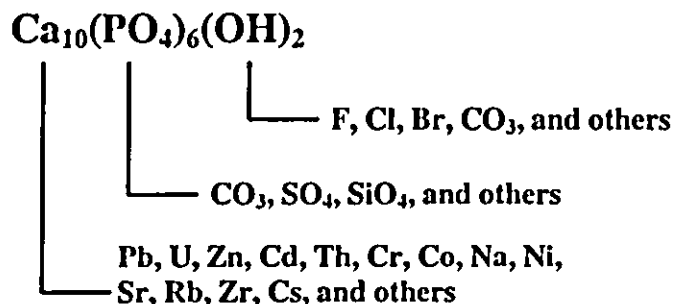


2.0 TREATMENT TECHNOLOGY DESCRIPTION

All of the technologies considered for ^{90}Sr removal from groundwater at 100-NR-2 use apatite as the sequestering agent, differing only by emplacement method. This section describes apatite in general and the properties that make it an excellent sequestering agent, includes a brief description of the different forms of apatite that are commercially available and have been used in bench testing, and provides a detailed description of the aqueous injection technology.

2.1 General Characteristics of Apatite

Apatite is a natural calcium phosphate mineral occurring in the earth's crust as phosphate rock, and is a primary component in the teeth and bones of animals. Apatite minerals sequester elements into their molecular structures via isomorphic substitution, whereby elements of similar physical and chemical characteristics replace calcium, phosphate, or hydroxide in the hexagonal crystal structure. Because of the numerous substitution possibilities, more than 300 apatite minerals are known to exist (Nriagu and Moore, 1984). The form of apatite without any substitution is known as hydroxyapatite (or hydroxylapatite), the chemical formula of which is shown below along with some of the more common substitution possibilities.



Apatite minerals are very stable and practically insoluble in water (Wright, 1990; Wright et al., 2004). The solubility product of hydroxyapatite is about 10^{-44} , while quartz crystal, which is considered the most stable mineral in the weathering environment, has a solubility product (K_{sp}) of 10^{-4} (Geochem Software, 1994). Strontiapatite, formed when all the Ca is replaced by Sr (or ^{90}Sr), is 10^7 times less soluble than hydroxyapatite (Verbeeck et al., 1977).

Apatite can remove soluble Sr and ^{90}Sr from groundwater both during and after its formation:

- Via precipitation of Sr in solution with PO_4 anion. Precipitation directly from solution, or homogeneous nucleation, generally occurs only at very high metal concentrations; that is, greater than 10 parts per million (ppm). However, apatite will act as a seed crystal for the precipitation of metal phosphates at much lower concentrations (Ma et al., 1995). The apatite itself serves as a small, but sufficient source of phosphate to solution, and with low concentrations of cations such as Sr or Ca, heterogeneous nucleation occurs on the surface of the apatite seed crystal (Lower

et al., 1998). Over time, the precipitated metals are sequestered into the apatite crystal matrix.

- Via substitution of Sr into the structure of mineral apatite. Sr and Ca are both alkaline earth metals with a 2+ charge, and both compete for the same lattice sites in the apatite structure. Because Ca is more prevalent in the earth's crust, it is more common in apatite. However, the substitution of Sr for Ca in the crystal structure is thermodynamically favorable, and in the presence of high enough concentrations, Sr will replace Ca.

Although the rate of metal incorporation into the apatite crystal lattice can be relatively slow, on the order of days to years, the precipitation reaction is nearly instantaneous on the molecular scale. Initially, the precipitate formed is amorphous apatite; however, within several days it will transform into a more stable apatite crystal.

It should be noted that stable strontium and other competing cations in groundwater, especially the divalent transition metals (e.g., Cd, Zn, Fe, Pb, Mn, etc.), can also be incorporated in the apatite structure. The average concentrations of stable strontium and competing cations present in groundwater will dictate the mass of apatite needed for long-term sequestration. For the NR-2 site, the average soluble (filtered) stable strontium concentrations for wells located between the shoreline and the 1301-N and 1325-N cribs for the period 1995 to the present is 270 ppb. The sum of the available average concentrations for the metals indicated in Section 2.1 is about 200 ppb (Appendix A).

The effect of competing cation concentrations is to reduce the in situ apatite longevity for a given mass loading. In order to achieve a desired longevity (e.g., a 300-year period during which most of the ⁹⁰Sr will have decayed), loading must be increased to account for the competing cation effect.

2.2 Mineral Apatite

Vertical hydrofracture and air injection emplace existing mineral apatite particles into the subsurface, while in aqueous injection, apatite is precipitated in situ from chemical precursors in aqueous form. The advantage of aqueous injection is that it has the potential to create a larger treatment zone surrounding the point of injection than the other technologies. Because of the potential to extend the treatment zone to the shoreline where aquatic biota are exposed, aqueous injection is the focus of this initial TTP. However, the other technologies may be field-tested in the future if aqueous injection does not perform as expected, or if additional sequestration capacity is needed.

Various forms of mineral apatite are commercially available, with potentially significant differences in properties that may affect the success of a site-specific field application. To determine which form of apatite would be the best choice for ⁹⁰Sr removal at 100-NR-2 (considering capacity, stability, cost, etc.), bench testing was conducted on several forms of apatite, including fish bone, cow bone, and mineral apatite. A brief description of each follows:

- Fish bone apatite is available in large quantities under the trade name of Apatite II from PIMS NW, Inc., Carlsbad, New Mexico. The physical structure of fish bone is largely amorphous, because fish skeletons are not required to bear significant weight. The crystalline apatite exists as random nanocrystals, within the amorphous or glassy matrix of the bone, and has many pores and capillaries that greatly increase the available surface area.
- Bone char and bone ash are two different cow bone-derived materials that have potential application at 100-NR-2, available from the Ebonex Corporation in Michigan. Bone char is heated at approximately 1,000 °C in an inert atmosphere that carbonizes organic material and results in black charcoal that makes up approximately 10 percent by weight of the finished material¹. Bone ash is produced in a similar manner except that the material is fired in the presence of oxygen at 1,100 °C, resulting in oxidation of organic matter to carbon dioxide and removal of carbon from the final material.
- Mineral apatite can be found in many phosphate rock sources mined in the U.S. for use in commercial fertilizer production. Mined from deposits that are millions of years old, they are stable minerals, but vary widely in chemistry, and may contain significant levels of Sr. Phosfill® material from North Carolina is typically much lower in trace metals than phosphate rock from the western U.S. (Crannell, 2005).

Characterization studies and column tests were initiated on the most promising forms of apatite to verify vendor performance data and statements. Results will be presented in a separate addendum.

2.3 Aqueous Injection of Apatite Precursors

Aqueous injection results in a dispersed zone of apatite precipitated in a treatment zone surrounding (and downgradient of) the injection points. Rather than physical placement of a solid apatite mineral in the subsurface, this technology involves the injection of the chemical components of apatite—principally calcium and phosphate—and then precipitation of the mineral in the formation. It is based on an approach recently published by Moore et al. (2004).

Apatite minerals are sparingly soluble, and calcium phosphate solids precipitate rapidly when any appreciable amounts of free calcium and dissolved phosphate are mixed. By using citrate to stabilize the solution of calcium and phosphate, the chemicals are able to migrate some distance from the point of injection before they precipitate, following microbial degradation of the citrate-complexing agent. The citrate acts as a chelating agent and forms stable complexes with dissolved calcium, reducing the free (uncomplexed) Ca^{2+} concentration in solution, and increasing the apparent solubility of the calcium/phosphate mixture. For example, the solution described in Table 2-1 was used by Moore et al. (2004) and was reported to be stable (without precipitates) for over 36 hours.

¹ Ebonex Corporation. <http://www.ebonex.com/> (address verified on November 8, 2005).

Table 2-1. Solution Used for Apatite Formation in Soils (Moore et al., 2004)

Chemical	Concentration	Remarks
Sodium Citrate (Na ₃ C ₆ H ₅ O ₇)	100 mM	
Calcium Chloride (CaCl ₂)	50 mM	
Sodium Hydrogen Phosphate (Na ₂ HPO ₄)	40 mM	
Ammonium Nitrate (NH ₄ NO ₃)	10 mM	Nitrogen source used to stimulate microbial activity
Potassium Hydroxide or Perchloric Acid (KOH and HClO ₄)	Negligible.	Used as needed to adjust solution to pH 7.5

For the remedy, a solution such as the one presented in Table 2-1 is prepared and then injected into the formation. As indigenous microorganisms degrade the citrate (this is an easily metabolized carbon source), the resulting increase in free calcium will result in precipitation of calcium phosphate solids in the aquifer (see Figures 2-1A and 2-1B). The specific steps of this remediation technology are:

- 1) Injection of Ca-PO₄-citrate solution (with a Ca-citrate solution complex).
- 2) In situ biodegradation of citrate resulting in apatite [Ca₅(PO₄)₃(OH)] precipitation and coprecipitation of ⁹⁰Sr in pore fluid and solids in the treatment zone.
- 3) Adsorption of ⁹⁰Sr by the apatite surface (i.e., new ⁹⁰Sr migrating into the treated zone from upgradient sources).
- 4) Apatite recrystallization with ⁹⁰Sr substitution for Ca (permanent).
- 5) Radioactive decay of ⁹⁰Sr to ⁹⁰Y to ⁹⁰Zr.

In studies over the past 5 years, Robert Moore (SNL) demonstrated that citrate biodegradation/apatite precipitation occurs in several sediments, resulting in the sequestration of U, Tc, Sr, and Pb. Laboratory bench studies at PNNL and SNL during 2004 and 2005 were focused on determining if this technology could precipitate sufficient apatite at 100-NR-2 to immobilize ⁹⁰Sr in both the near-term as well as for 300 years, and if the ⁹⁰Sr removal rate would be rapid enough. Additional studies are underway to assess the potential impact of other cations in NR-2 groundwater on barrier longevity (i.e., by substitution for calcium in the apatite structure).

The solids are initially amorphous; however, laboratory tests show that they age to form crystalline apatite on a time scale of weeks. The apatite will reflect the chemistry at the time of precipitation and contain varying proportions of cations (calcium, magnesium, sodium, and strontium) and anions (phosphate, carbonate, and hydroxide) depending on their solution concentrations. In this respect, the physical and chemical properties of the synthetic mineral are not as well-characterized as commercially available apatite; however, the material is expected to remain effective at sequestering ⁹⁰Sr. Mechanisms of sequestration include strong

sorption onto the mineral surface and isomorphic substitution within the structure of the mineral.

As previously noted, the advantage of the aqueous injection remedy is the prospect of delivering apatite over a broad area of the near-shore aquifer, possibly reaching to the river. As currently envisioned, the aqueous injection remedy involves creating a zone of apatite in the aquifer via a series of groundwater injection wells. Figure 2-2 illustrates an array of injection wells and the initial distribution of injected chemicals. The zone will extend from the initial point of injection in response to the groundwater flow regime and the microbial degradation rate. The resulting treatment zone will decrease the ^{90}Sr pore fluid concentrations and flux by sequestering ^{90}Sr currently in this area, and by intercepting ^{90}Sr as it migrates into the zone from upgradient sources. The broad treatment zone will also provide a longer residence time for adsorption and sequestration of upgradient sources.

If successful, the net effect of the treatment would be to decrease contaminant flux to the river by sequestering ^{90}Sr until radioactive decay lowers ^{90}Sr activity to acceptable levels.

Figure 2-1A

Aquifer Prior to Injection of Apatite Forming Chemical Solutions

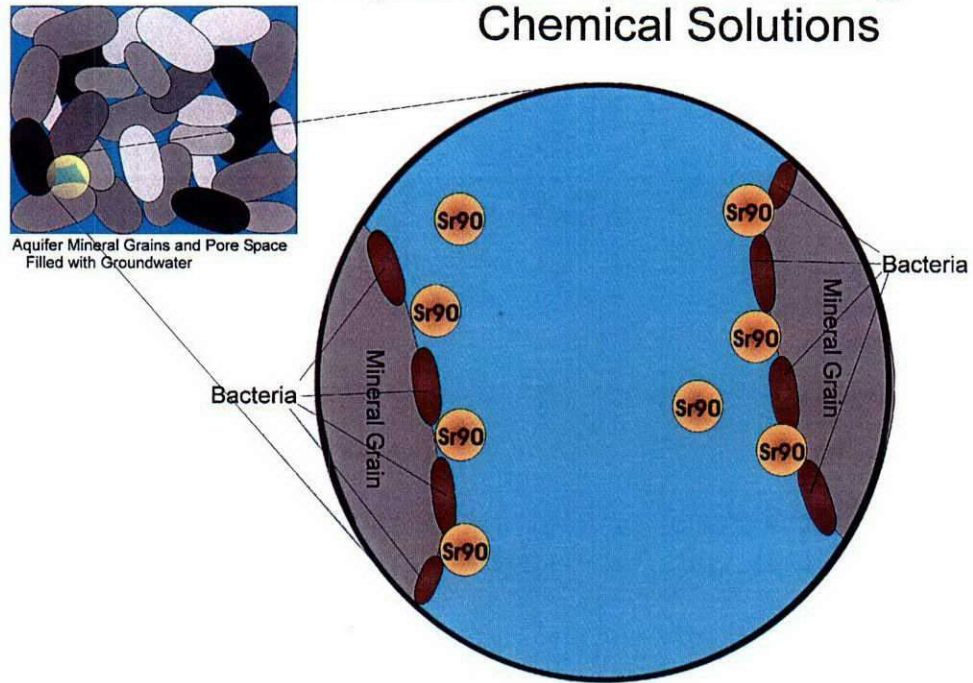


Figure 2-1B

Fixation of Sr90 by Apatite Formation

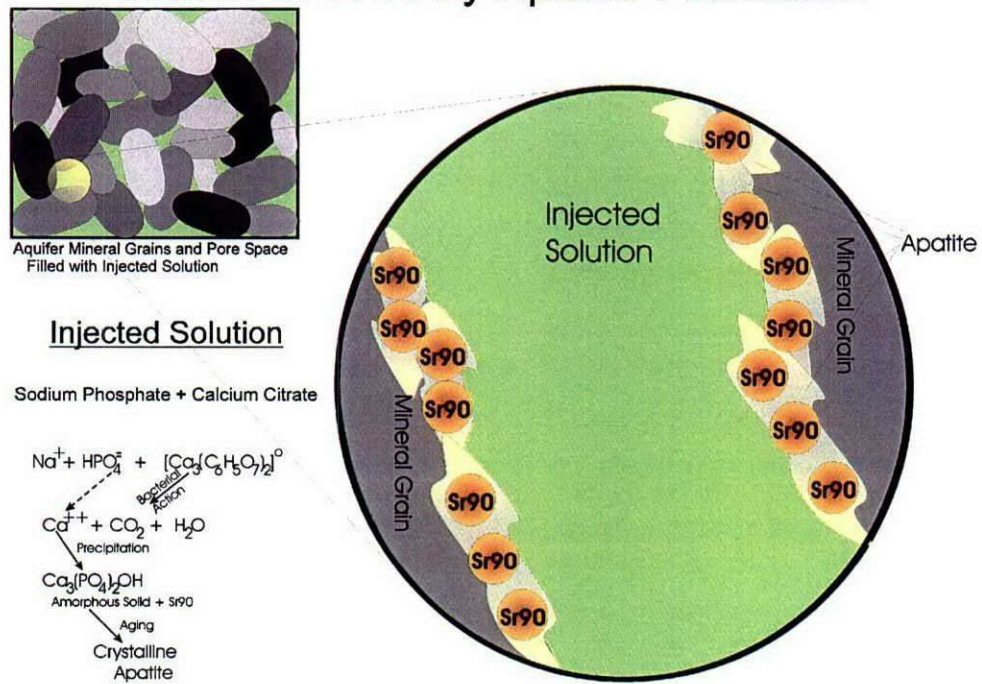
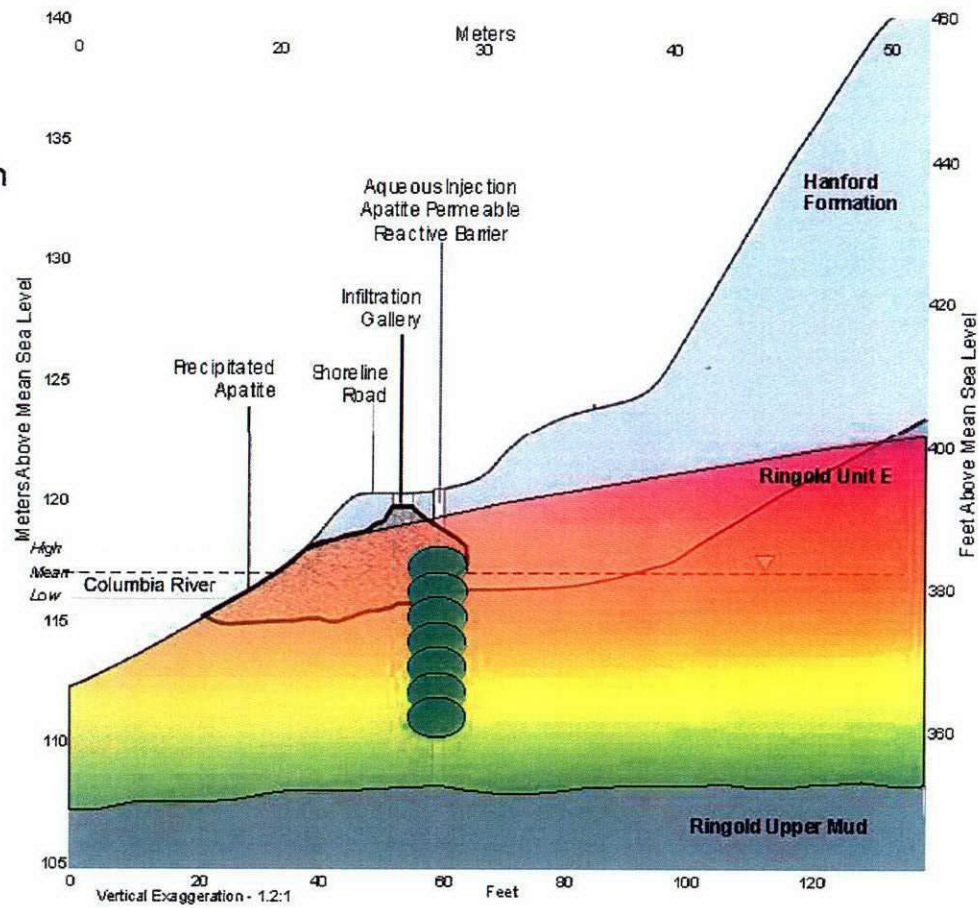


Figure 2-2

Alternative Interim Remedy: Apatite Sequestration

- Well injection treatability test to address upper aquifer (FY 2006)
- Apatite chemical infiltration pilot test in FY2007 to treat vadose zone.
- Target highest clam/porefluid Sr-90



2.4 Potential Chemical Effects Issues

Bench tests in 2004 and 2005, described in Section 3, were conducted to evaluate in situ apatite formation and its effectiveness, identify any unintended consequences, and address concerns raised during public briefings and workshops.

Salt Leaching Effect. One potential consequence may be increased mobility of ^{90}Sr along the margins of a treatment area. Identified as the "salt effect," the concern is that the injection solution would have higher salts than the groundwater in the treatment area. Some of the dissolved salts such as sodium and chloride do not participate in the precipitation reactions and remain in solution after calcium and phosphate precipitate. As the relatively high total dissolved solids (TDS) water migrates away from the treatment zone into an area where ^{90}Sr has not been sequestered by apatite, cations exchange with ^{90}Sr (or other cationic contaminants) adsorbed on aquifer sediments. Thus, the salt effect would result in increased pore water concentrations of ^{90}Sr downgradient of the treatment area.

To mitigate this potential problem, the apatite precursors will be introduced in steps, as discussed further in Section 3. The first step involves injection of a dilute apatite solution that results in a minimal salt effect, but emplaces sufficient apatite to sequester the ^{90}Sr mobilized by subsequent injections. In the second step, a concentrated solution is introduced. This step may be divided into two or more injections; however, the goal will be to emplace enough apatite to treat the ^{90}Sr carried into this area via groundwater over the next 300 years.

Diesel-Related Chemical Effects. A large diesel spill occurred just upstream from the ^{90}Sr plume area during the 1960s. As much as 1 foot of floating product was observed in nearby monitoring wells in the past (e.g., N-18). Today there is no evidence of free product remaining; however, elevated dissolved iron (up to 24,000 ug/L) and depleted oxygen occurs in well N-18, indicating reducing conditions in the aquifer impacted by the diesel spill. Also, depleted oxygen and elevated iron in shallow aquifer tubes near the shoreline in front of the past spill area were found during summer 2005. A question was raised during the October 2005 public workshop on possible effects of the diesel and related degradation byproducts on the proposed apatite treatment remedy.

One possible impact considered was competition of the dissolved iron for the sequestration sites in the emplaced apatite. Although this is theoretically possible, the specific impact of dissolved iron on apatite performance has not been evaluated. However, a monitoring well (N-96A) located near the river bank at the center of the past diesel spill site indicates a maximum dissolved iron concentration of ~100 ug/L occurred in the past with less than 50 ug/L in 2005. Thus, it is unlikely that dissolved iron concentrations in the proposed treatment zone will be higher than in well N-96A. Two new monitoring wells drilled for the planned treatability test will be used to verify the expectation that dissolved iron concentrations are not elevated in the proposed apatite treatment zone. Laboratory studies will be needed to evaluate the long-term implications of diesel and potentially elevated dissolved iron.

(Note: Dissolved iron, both ferrous and ferric, were measured in purge water samples from new wells N-122 and N-123 during a vertical velocity profile test in December 2005. All samples were less than 10 ug/L).

Water Quality Impacts. The chemical byproducts from the apatite precipitation process include simple salts (sodium and calcium chloride) and small amounts of agricultural type chemicals (sodium phosphate and ammonium nitrate) and any remaining unreacted calcium citrate. The initial tests will be conducted using more dilute solutions (nominally 0.01 molar) than used for initial lab studies (~0.1 molar). Thus, a conservative approach will be used during the initial field treatability testing. The array of existing aquifer tubes at the shoreline covering the planned 300-foot (91-meter) treatment zone will be used to monitor the concentrations of reaction products. Dilution by river water is expected to greatly reduce the salt concentrations at the river-riverbed interface. The non-hazardous nature of these food (e.g., citrate) and agricultural-type chemicals are highly unlikely to have a negative impact on the near-shore biota. The residual chemical plume from the treatment zone will occur as a temporary pulse that will dissipate and mix with river water in the streambank storage zone and as it discharges through the riverbed gravels. Evaluation of the monitoring data from the aquifer tubes will be used to guide future treatment regimes and injection protocol.

Creation of a New Buried Waste Site. Long-term accumulation of ^{90}Sr by the apatite emplaced along the shoreline could be considered creation of a new buried waste site along the river. The objective of the sequestration barrier is to fix the migrating ^{90}Sr in place and thereby reduce the flux to the near-shore zone. Accumulation of ^{90}Sr in the treated zone represents trading continued exposure of near shore biota for fixation of the contaminant where it is not in contact with biota. One important mitigating factor is that the shoreline along the central portion of the ^{90}Sr plume is protected with rip-rap and is thus protected from major erosional events. Thus it is highly unlikely that the buried apatite could be eroded under even extreme hydrologic event scenarios.

In addition, the area in question is already contaminated with ^{90}Sr so it is not really a question of creating a new buried waste site. The only difference will be the capture of ^{90}Sr in aquifer pore fluid that passes through the barrier and remains in the treatment zone until it decays to insignificant amounts. For example, the total amount currently estimated in the aquifer is about 0.8 Ci. If this amount is captured in the volume of aquifer sediment treated by the in situ apatite PRB, the resulting average concentration would be approximately 200 pCi/g (for a 300-foot barrier emplacement). This concentration is not much higher than concentrations currently observed in shoreline sediments. Considering decay, there would be less than 20 pCi/g left in 100 years, which is near the cleanup standard. The issue of whether or not this constitutes a new waste site that needs a Waste Information Data System (WIDS) designation can be evaluated, if necessary, for the final remedy.

2.5 Testing

PNNL conducted bench studies in 2004 and 2005 to determine if this technology could precipitate sufficient apatite in 100-N area sediments and if the ^{90}Sr removal rate would be rapid enough to immobilize ^{90}Sr for 300 years. Results are presented in Section 3. Given the favorable laboratory results, a pilot test involving a single injection well and multiple

monitoring points will be conducted to confirm apatite formation in the field and to determine optimum injection volumes and rates to achieve a 300-foot treatment zone. (Additional details and a schedule of planned activities for 2006 are presented in Section 4.) If the treatability test shows that this technology will precipitate apatite in 100-NR-2 sediments in situ, and that ^{90}Sr concentration in groundwater is reduced as a result, a second (and possibly third) round of injections to emplace the remaining balance of apatite treatment capacity may be required. If results from the initial treatability test are not favorable, then other options will be tested (e.g., PRB emplacement of apatite particles using vertical hydraulic fracturing or air injection).

3.0 AQUEOUS INJECTION BENCH STUDIES

Bench tests were conducted at SNL and at PNNL to demonstrate the feasibility of aqueous injection, and to quantify various processes involved in the technology. Studies at PNNL and SNL using 100-N area sediment addressed:

1. Aerobic and anaerobic citrate biodegradation pathways and rates
2. Amorphous and crystalline apatite precipitation in 100-N sediments
3. ^{90}Sr uptake in apatite-laden 100-N sediment
4. Depth profiles of ^{90}Sr and microbial population densities in the N-121, N-122, and N-123 borehole core sections
5. Adsorption properties of ^{90}Sr in treated and untreated sediments

Biodegradation rates and reagent distribution become critical injection design considerations when combined with the hydrodynamics of the near-shore zone that is subject to flow direction reversals and water table fluctuations in response to river stage. Adsorption studies are needed to define the expected capacity of the treated aquifer to sequester ^{90}Sr . This section describes these studies and discusses the significance of the results with relation to apatite formation, Sr sorption/desorption, and other issues.

3.1 Apatite Formation

As described in Section 2, this technology involves the injection of a Ca-PO_4 -citrate solution (with a Ca-citrate solution complex), into the aquifer. As the Ca-citrate complex biodegrades, free calcium is released and immediately precipitates with dissolved phosphate. The rates of citrate degradation and phosphate distribution are very critical to the success of this technology.

3.1.1 Citrate Biodegradation

Moore et al. (2004) at SNL conducted batch tests using 250 grams of soil from Los Alamos, New Mexico, amended with 150 ml of the solution described in Table 2-1. Citrate degradation was documented in the Ca/citrate/phosphate-treated soils within 80 hours (a sterilized batch of treated soils showed no citrate decay, confirming a microbial degradation pathway for this complexing agent).

Degradation Rates at Different Temperature and Concentration

Recent studies at SNL focused on the biodegradation rate of citrate at different citrate concentrations and at different temperatures in 100-N Hanford formation sediments (Table 3-1). Because the injection strategy will involve an initial low-concentration (~10 mM citrate) injection followed by higher concentration (~100 mM citrate), data are needed to describe the citrate biodegradation rate at different concentrations. The 100-N aquifer temperature varies seasonally from 14°C to 17°C, so citrate biodegradation rates are needed

at this aquifer temperature. Previous laboratory data for aerobic and anaerobic citrate biodegradation rates were for 15°C. Recent laboratory batch studies were conducted at 10°C, 15°C, and 21°C in order to develop the relationship between the citrate biodegradation rate and temperature.

Rates determined from experiments show that the citrate biodegradation rate increases with temperature (2.7x from 10°C to 25°C) and decreases with increasing citrate concentration (3.0x from 10 mM to 100 mM; Figure 3-1). The initial injections at 10 mM citrate and 15°C have an estimated half life of 50 h.

Figure 3-1. Citrate Biodegradation By Hanford 100-N Sediment at Different Temperature for Citrate Concentrations of: a) 10 mM b) 50 mM c) 100 mM

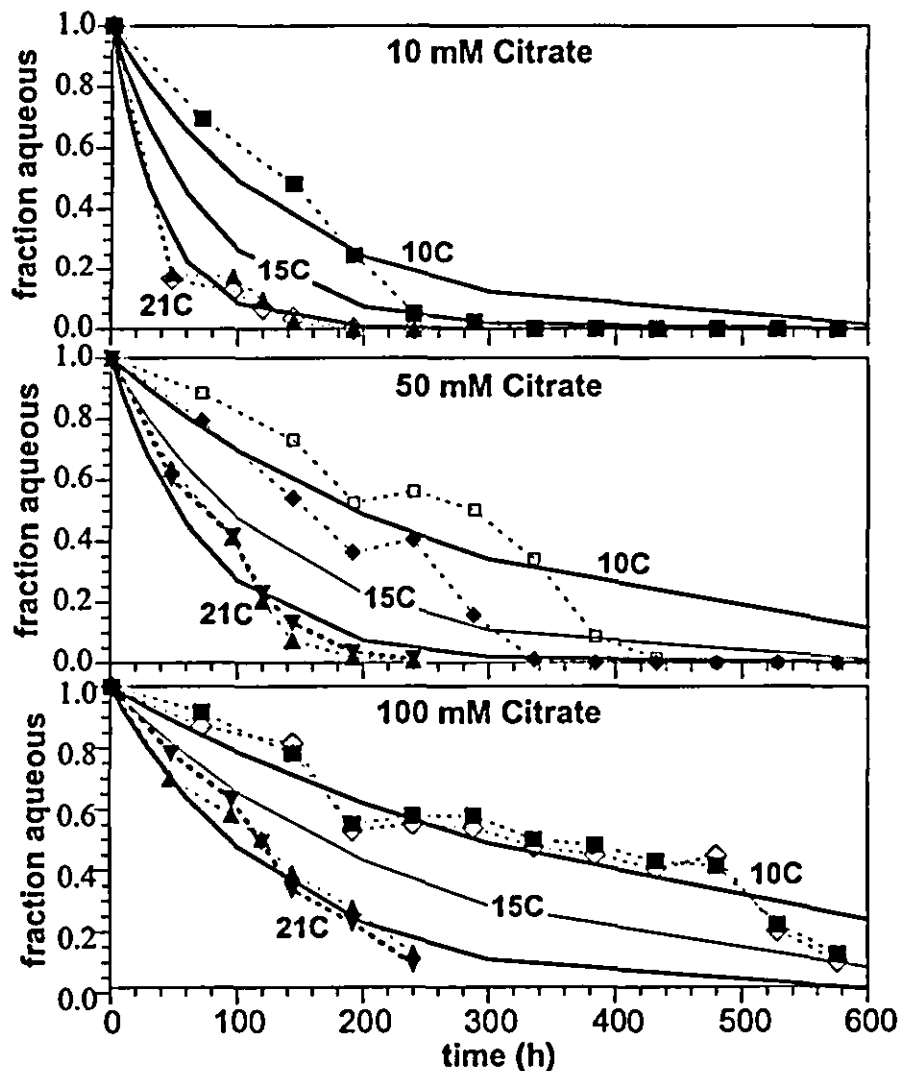


Table 3-1. Citrate Biodegradation Rates as a Function of Temperature and Initial Citrate Concentration

Concentration, mM	Rate Constant, 10°C	Rate Constant, 15°C	Rate Constant, 21°C
10	0.0071	0.013	0.025
50	0.0074	0.0036	0.013
100	0.0024	0.0042	0.0075

Influence of Temperature and Concentration on Citrate Biodegradation Rate

Citric acid is used by many organic systems as part of the TCA (Krebs) photosynthetic process, where the citrate (a C6 organic acid) is converted to C6, C5, and C4 organic acids producing CO₂ and H⁺, then cycled from oxaloacetic acid (C4) to citric acid (Bailey and Ollis, 1986). Citrate can also be further degraded to acetic acid (C2), formaldehyde, formic acid (C1), and CO₂. For the purpose of this study, citrate is used to complex Ca, so only the decrease in citrate concentration (by biodegradation) is of significance, as the lower molecular weight organic acids only form weak complexes with Ca.

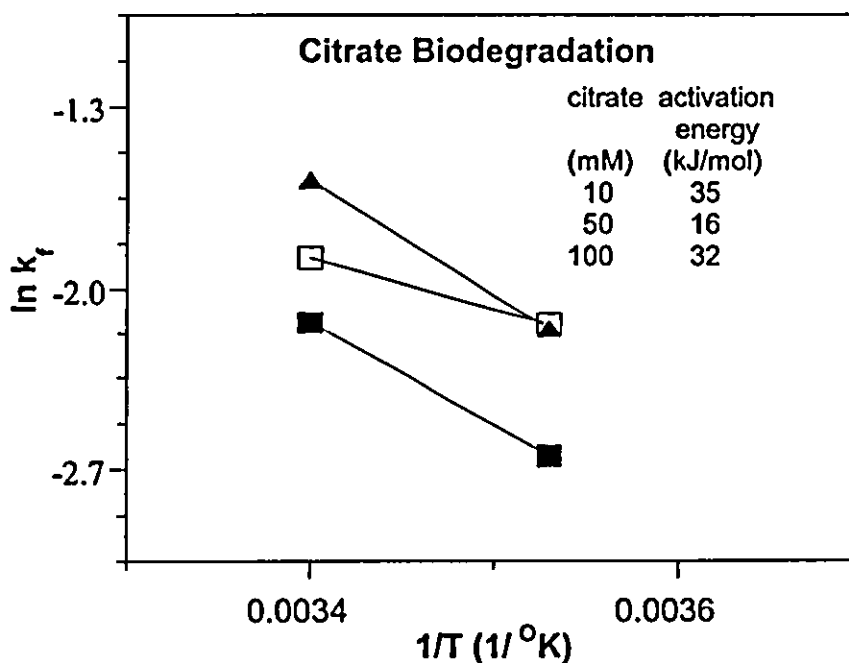
Two different modeling approaches at PNNL were considered to quantify citrate biodegradation: a first-order model, and a Monod model. A first-order model is an empirical approach that describes citrate removal with a single reaction rate coefficient. A Monod model is also an empirical approach that describes citrate removal externally to microbial organisms with a similar mathematical form of enzyme degradation (Michaelis-Menton kinetics). Monod kinetics is used when the observed data clearly show a considerable slowing of reaction rate at low concentration that cannot be accounted for using the simpler first-order kinetic model.

Citrate biodegradation experiments show a slower rate at colder temperature and at higher citrate concentration (Figure 3-1, Table 3-1). At 10 mM citrate concentration, citrate was not detectable by 200 h (21°C) to 300 h (10°C, Figure 3-1a). At 50 mM citrate concentration, citrate was nondetect by 250 h (21°C) to 450 h (10°C, Figure 3-1b). At 100 mM citrate concentration, a small amount of citrate remained at 300 h (21°C) to 600 h (10°C, Figure 3-1c). At each concentration, duplicate experiments showed similar results.

A first-order model (lines, Figure 3-1) showed good fits, and indicated that in some cases, citrate biodegradation may be somewhat more rapid at lower concentration than a first-order approximation. For example, the 100 mM citrate data at 10°C (Figure 3-1c) showed a good first order fit to 500 h, but then citrate more rapidly degraded. This effect is observed for all citrate concentrations at 10°C, but not at 21°C. A Monod kinetic model would describe the data equally as well with small half-saturation constants, but would describe the data more poorly with higher concentration half-saturation constants, which would slow citrate biodegradation at low concentration, the opposite effect of that observed. Therefore, a pseudo first-order model was used to quantify the rate data (Table 3-1).

The citrate biodegradation rate was 3.0 x slower (10°C data) to 3.3x slower (21°C data) as the citrate concentration increased from 10 mM to 100 mM. The citrate biodegradation rate averaged 3.3x slower as the temperature decreased from 21°C to 10°C. The activation energy estimated from the reaction rate change with temperature is 35 kJ/mol (10 mM citrate), 16 kJ/mol (50 mM citrate), and 32 kJ/mol (100 mM citrate). These activation energies indicate the rate is controlled by the biochemical reaction and not diffusion, which is expected (Figure 3-2).

Figure 3-2. Arrhenius Plot of Citrate Biodegradation Rates versus Absolute Temperature, with Calculated Activation Energy

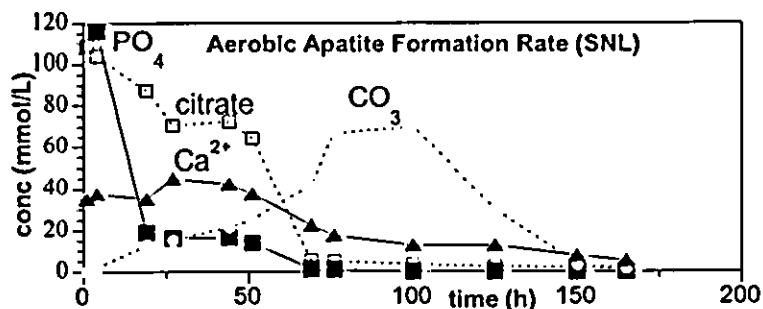


Aerobic vs. Anaerobic Degradation

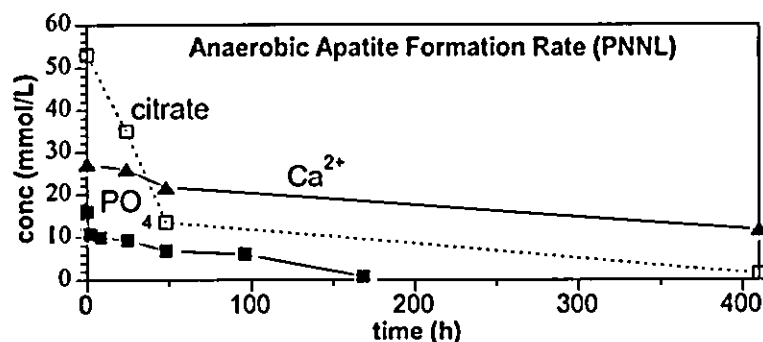
In batch and 1-D column systems, SNL and PNNL showed that citrate biodegradation to CO₂ occurred within 75-100 h in aerobic systems (Figure 3-3a), and to formate and acetate within 100-200 h in anaerobic systems (Figures 3-3b and 3-3c). In the 100-N Ringold portion of the aquifer, most of the citrate biodegradation will occur anaerobically, given the relative concentrations of citrate to oxygen. In the Hanford formation, the uppermost portion of the aquifer, degradation will most likely be aerobic.

Figure 3-3. Apatite Precipitation Rates (Aerobic and Anaerobic), and Citrate Biodegradation Rate (Anaerobic)

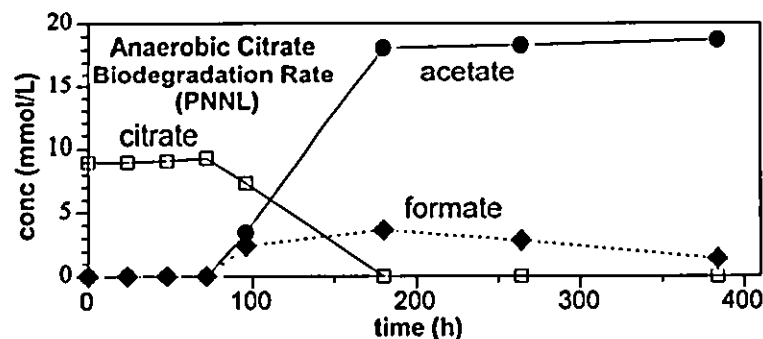
a) Apatite Precipitation Rate in Aerobic System (SNL Exp.) (CO_2 reported as CO_3)



b) Apatite Precipitation Rate in Anaerobic System (PNNL Exp.)



c) Citrate Biodegradation Rate in Anaerobic System (PNNL Exp.)

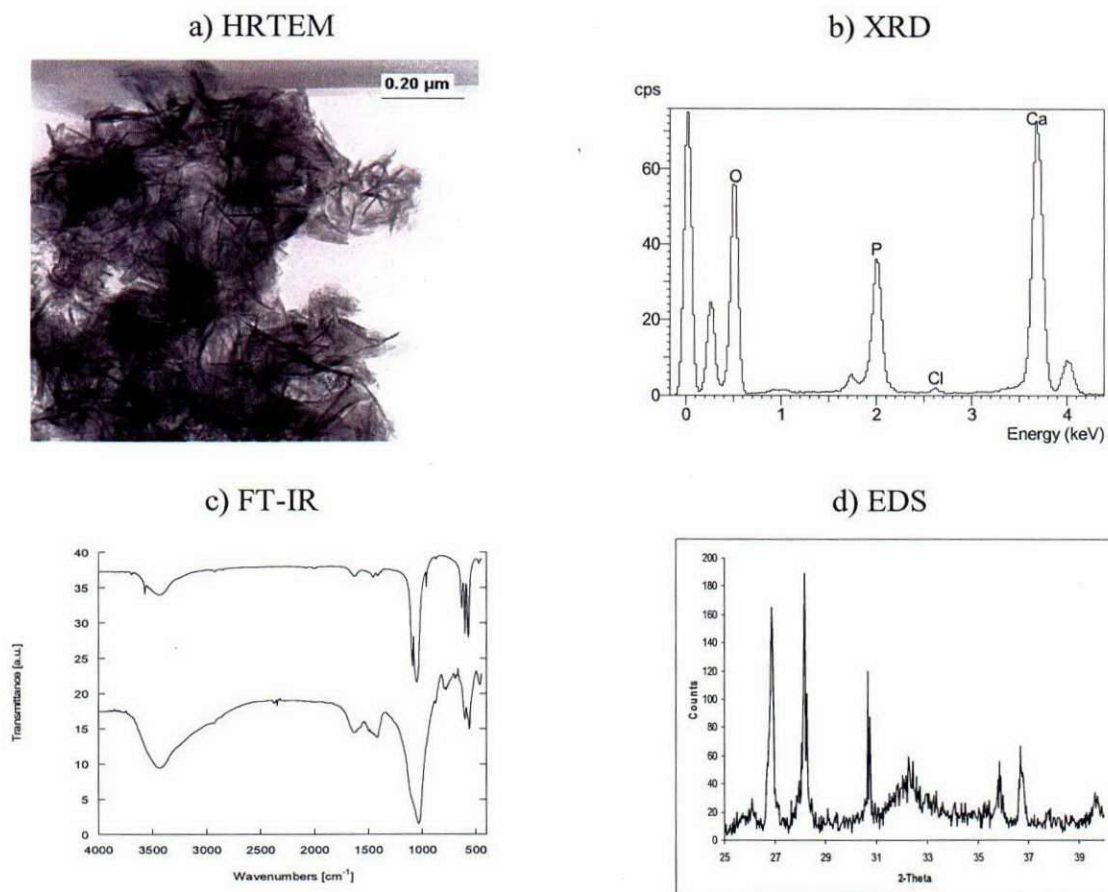


3.1.2 Apatite Precipitation

SNL observed the formation of apatite precipitate in 100-N columns. Using x-ray diffraction and other solid phase microprobe techniques, investigators at SNL observed that the initial precipitate within 100 h is amorphous, but then crystallizes within 2 to 4 weeks to hydroxyapatite (Figure 3-4). Batch experiments varying mixing, trace nutrient addition, and nitrate addition showed similar results. Figure 3-4a shows nanosize apatite crystals formed in

sediment through precipitation from aqueous solution from citrate biodegradation in a batch system with 100-N sediment and excess oxygen (simulating vadose zone conditions).

Figure 3-4. Nanocrystalline Apatite Formed in Hanford Sediment by Microbially Mediated Ca-Citrate Degradation in the Presence of Aqueous Phosphorous



Apatite Precipitate Characterization (SNL). The mineral apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$, is the most abundant, ubiquitous phosphorous-bearing mineral on earth and is used broadly by earth scientists in the study of igneous, metamorphic, and sedimentary petrogenetic processes (Hughes and Rakovan, 2002). In addition to its geologic utility, apatite is used in industry for such diverse applications as a source for fertilizer, a component of fluorescent lamps and lasers, as nuclear waste forms, and in biomedical applications (G. Waychunas, 1989; R.C. Ewing, 2001; J.C. Elliot et al., 1973). In fact, hydroxyapatite is the primary mineral component in bone and teeth (J.C. Elliot et al., 1973). The apatite structure and its chemical facility provide the basis for its broad and varied application.

Apatite can refer to three specific end-member minerals: fluorapatite, chlorapatite, and hydroxyapatite. All can be viewed as slight modifications of the $P6_3/m$, $Z=2$ structure. For a complete description and structural details see Hughes et al. (1989). Several features of the

structure are noteworthy. PO_4 -tetrahedra are found in a hexagonal arrangement within the (001) planes defining columns parallel to the z-axis. The PO_4 oxygens are coordinated with Ca in two different sites. The Ca1 site is intercalated between the (001) planes and coordinated to nine oxygens. The Ca2 site is coordinated to six oxygens and the column anions (typically F, Cl, or OH). The Ca2 site shows the greatest degree of structural distortion upon chemical substitution. The apatite structure exhibits extensive solid solution with respect to both cations and anions. Metal cations (e.g., actinides, K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Fe) substitute for Ca and oxyanions (e.g., AsO_4^{3-} , SO_4^{2-} , CO_3^{2-} , SiO_4^{4-} , CrO_4^{2-}) replace PO_4^{3-} through a series of coupled substitutions to preserve electroneutrality (Hughes and Rakovan, 2002).

Multiple characterization techniques were employed to assess the crystal chemistry of the apatite formed by the microbial digestion of Ca-citrate in sediment from the Hanford Site. High resolution transmission electron microscopy (HRTEM) and X-ray powder diffraction (XRD) were used to assess apatite crystallinity and to document the transformation from an amorphous calcium phosphate to nanocrystalline apatite. Energy dispersive (EDS) and Fourier transform-infrared (FT-IR) spectroscopy were used to analyze the chemical constituents. The apatite was formed in sediment collected from 100-N by treatment with a solution of 50 mM sodium citrate, 25 mM calcium chloride, 20 mM sodium phosphate and nutrients for microbial activity at pH 7.4. Blade-like crystals in an amorphous matrix are approximately 0.1 μm in size (Figure 3-4a). This was consistent with the observed broad overlapping peaks in the XRD pattern at 2 microns of approximately 32°C, a typical characteristic of poorly crystallized apatite (Figure 3-4b). The remaining peaks in the XRD correspond to components of the sediment. FT-IR spectra are given for pure hydroxyapatite (top spectrum) produced by precipitation and heat treatment at 700°C and calcium phosphate precipitates in the 100-N sediment after 1 month (bottom spectrum). The lower resolution of the PO_4 bands confirms the lower crystallinity of the sample, as observed by both HRTEM and XRD. The bands at 1,455 cm^{-1} and 879 cm^{-1} indicate the presence of carbonate in the apatite structure. The HRTEM-EDS spectrum identifies calcium and phosphate as the major components with a stoichiometric apatite ratio of approximately 5:3.

Apatite Formation Reaction Rates and Design Considerations

Apatite formation reaction rates, and their relation to the complex groundwater flow dynamics associated with the near-river environment at 100-N, must be considered in the injection design analysis (see Section 4) for field deployment of the apatite PRB technology. Laboratory column experiments showed that amorphous apatite formed within 75 to 200 hours, with subsequent formation of crystalline apatite occurring within 2 to 4 weeks post-injection. These apatite formation rates, and their relation to groundwater flow conditions, illustrate one of the important design constraints that must be considered during development of the treatment zone emplacement approach. The selected injection design must allow for the apatite-forming reagents to be in contact with the targeted treatment zone for a sufficient time period to form the desired apatite distribution. This and other design constraints will be evaluated based on laboratory testing results and simulation results from a flow and reactive transport model. The resulting injection design will be documented in the field test instructions issued prior to commencement of field activities.

3.2 ⁹⁰Sr Sorption/Desorption

A second critical process in this technology is the uptake of ⁹⁰Sr by apatite. A number of experiments have been conducted at SNL and PNNL to assess the Sr sorption properties, adsorption rate, and the adsorption mechanism in apatite-treated soil. Because aqueous injection will result in higher groundwater salt concentrations, the influence of ionic strength on ⁹⁰Sr desorption from untreated and apatite-treated soil was also the subject of a series of experiments by PNNL.

3.2.1 Sorption Capacity

Researchers at SNL conducted batch tests to assess the Sr sorption properties of the apatite-treated soil versus untreated controls and a phosphate-only treatment (Figure 3-5). The sorption studies were conducted in a background of 0.1 M KNO₃. As shown, the apatite treatment enhanced strontium sorption, when compared to the other treatments and controls. Nearly 99 percent of the Sr was sorbed to the apatite-treated soil in the concentration range that will likely to be encountered in the field (2×10^{-6} mol/L or 0.2 mg/L). The partitioning between solid and liquid phases was rapid, reaching equilibrium within 1 day of contact.

Figure 3-5. Sr Sorption in Apatite-Treated Soil

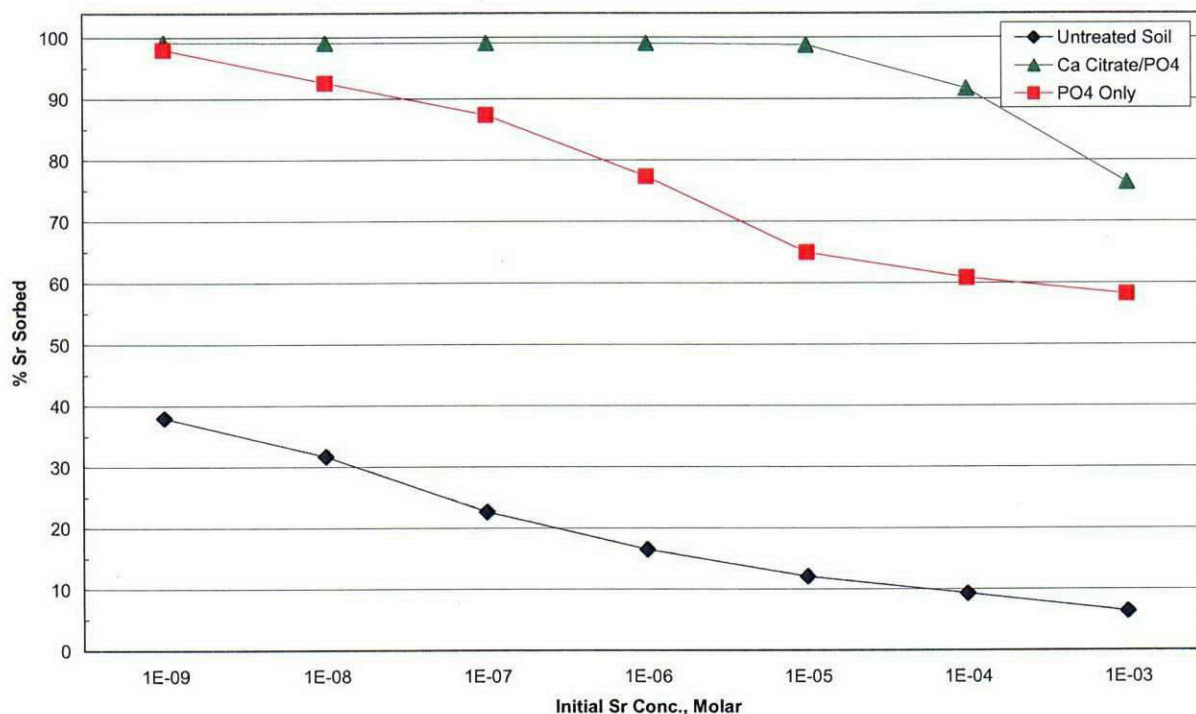


Table 3-2 presents the sorption/desorption data reported by Moore et al. (2004). As shown, significantly less Sr is removed from the apatite-treated soils when compared to the other soils, and the rate of desorption changes very little over time.

Table 3-2. Results of Strontium Sorption/Desorption Experiments
From Moore et al. (2004)

[Sr] Initial (molar)	Percent Sr Sorbed	Percent Desorbed After		
		1 week	1 month	6 months
Untreated Soil				
1×10 ⁻⁹	38.0	20.4	26.8	26.6
1×10 ⁻⁸	31.7	22.3	23.9	24.0
1×10 ⁻⁷	22.6	25.8	28.0	28.7
1×10 ⁻⁶	16.5	26.9	31.4	34.0
1×10 ⁻⁵	12.1	27.5	29.1	32.5
1×10 ⁻⁴	9.3	38.9	44.7	46.3
1×10 ⁻³	6.4	41.1	56.2	57.3
Phosphate-Only				
1×10 ⁻⁹	98.0	15.6	29.0	24.8
1×10 ⁻⁸	92.5	18.0	20.0	29.0
1×10 ⁻⁷	87.3	22.3	28.9	31.0
1×10 ⁻⁶	77.3	24.0	27.8	27.0
1×10 ⁻⁵	64.9	23.0	22.0	26.9
1×10 ⁻⁴	60.8	21.0	26.3	29.5
1×10 ⁻³	58.2	22.5	32.1	33.6
Calcium Citrate/Phosphate				
1×10 ⁻⁹	99.2	0.1	0.1	0.2
1×10 ⁻⁸	99.1	1.1	1.0	1.2
1×10 ⁻⁷	99.1	1.7	3.2	3.6
1×10 ⁻⁶	99.1	3.1	3.4	3.6
1×10 ⁻⁵	98.8	5.6	5.9	5.9
1×10 ⁻⁴	91.7	6.9	7.0	7.9
1×10 ⁻³	76.4	11.2	10.2	11.1

3.2.2 ^{90}Sr Adsorption Rate as a Function of Ionic Strength

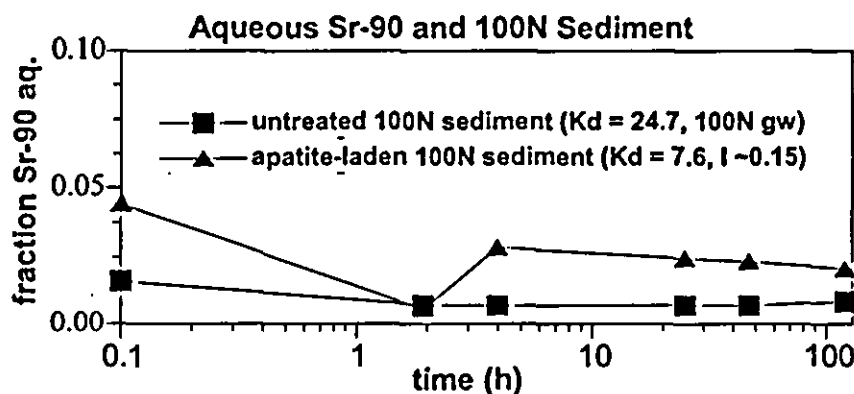
Laboratory experiments were conducted to measure the ^{90}Sr adsorption rate in untreated 100-N sediments and the ^{90}Sr uptake rate by apatite-laden sediments. Sequential experiments were used to remove the ^{90}Sr on the sediment surface to determine if the ^{90}Sr was held on the surface by ion exchange or was incorporated into the apatite structure.

Methods. Using the 100-N composite sediment (from 10 to 42-foot depth at well N-121) and 100-N groundwater (Ca/Sr ratio of 220/1) with the addition of 1 mCi of ^{90}Sr , two experiments were conducted. The first experiment used no additional amendments. In the

second experiment approximately 0.5 g of apatite was added, and the ionic strength was approximately 0.1 M (diluted from the original Ca, PO₄ citrate mixture).

Results. The adsorption equilibrium for the untreated sediment was reached within 2 h, resulting in a Sr K_d value of 24.7 cm³/g (Figure 3-6). Sediment extractions show that ⁹⁰Sr was retained by ion exchange, so it is not surprising that equilibrium was achieved relatively quickly. In the treated sediments, the solution ⁹⁰Sr continued to decrease even after 120 h. The apparent K_d at 120 h was 7.6 cm³/g, which was lower than the untreated sediment and resulted from the higher solution ionic strength.

Figure 3-6. Aqueous ⁹⁰Sr Sorption to 100-N Sediments



These results, showing the influence of major ions on Sr retention by Hanford sediments, are supported by previous work. Routson et al. (1981) reported a Sr K_d of 49 cm³/g in the presence of 0.001M NaNO₃, and a K_d of 16 cm³/g in the presence of 0.1M NaNO₃, or a 4x decrease in the K_d value with a 100x increase in molarity. In general, Sr²⁺ retention by ion exchange is controlled to a large extent by Ca²⁺ concentration in solution. A similar change in Ca²⁺ ionic strength (0.001 to 0.1) resulted in a 38x decrease in the Sr K_d value.

3.2.3 ⁹⁰Sr Sorption via Ion-Exchange versus "Sequestration"

It was hypothesized that untreated sediment sorbs Sr predominantly by ion exchange, while in apatite-laden sediments, Sr becomes more permanently sequestered over time. To test this hypothesis, untreated and apatite-laden 100-N sediments were treated by a sequence of solid phase extractions:

1. Extraction by 0.5M KNO₃ (released ions bound by ion exchange)
2. Extraction by 6 percent 0.05M ethylenediaminetetraacetic acid (EDTA) (released ions dissolved from carbonate)
3. Extraction by 4M HNO₃ at 80°C for 24 hours (ions dissolved from minerals)

Methods. Solid-phase extractions were conducted on three different sediments:

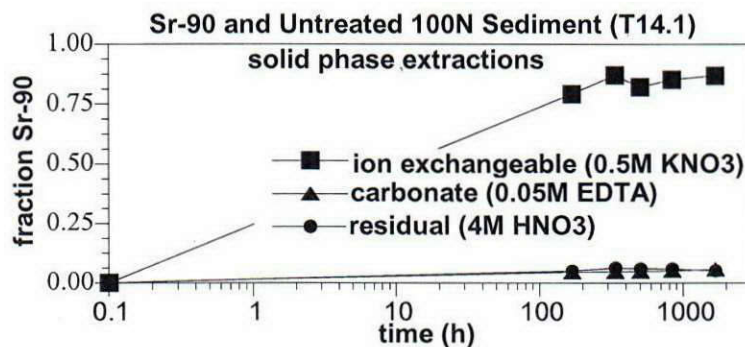
1. 100-N sediment from the 13-foot depth (which contains 80 pCi/g ⁹⁰Sr), ⁹⁰Sr solution added

2. Apatite-laden 100-N composite sediment, with ^{90}Sr solution added
3. 100-N sediment from the 13-foot depth (which contains 80 pCi/g ^{90}Sr), apatite precipitate added

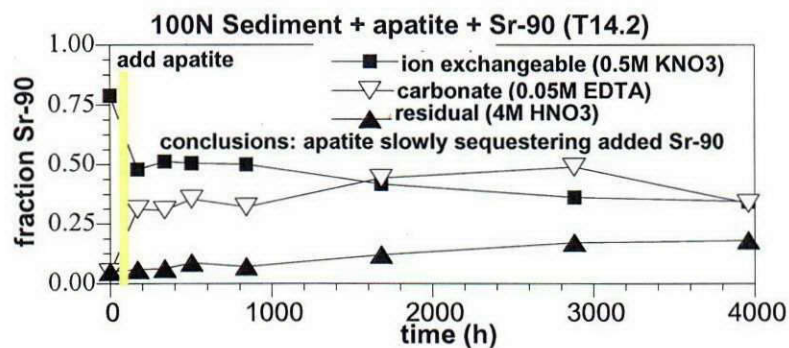
Results are presented in Figure 3-7.

Figure 3-7. Solid-Phase ^{90}Sr Extractions for:

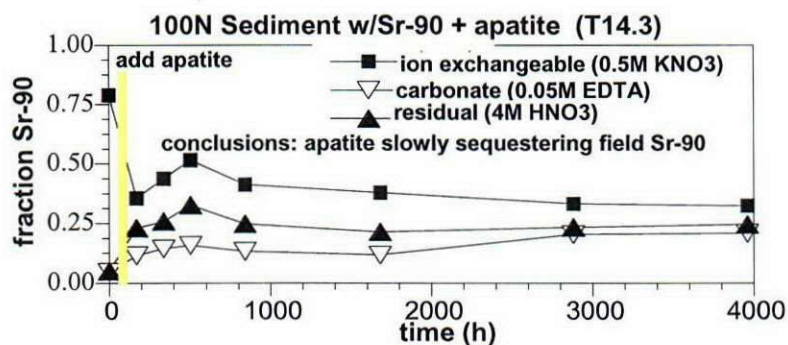
a) Untreated 100-N Sediment with ^{90}Sr added



b) ^{90}Sr and Apatite Addition to Sediment



c) Apatite Only Addition to 100-N Sediment (which Contains 80 pCi/g ^{90}Sr)



Results—Untreated 100-N sediments. Solid-phase extractions showed that ~86 percent of the ^{90}Sr on untreated sediments was released by ion exchange, about 6 percent was released by carbonate extraction, and about 6 percent by mineral dissolution extraction (see Figure 3-7a). The remaining 5 percent ^{90}Sr was aqueous. Therefore, ^{90}Sr was retained on untreated 100-N area sediments predominantly by ion exchange, as expected. Samples taken at weekly intervals to 10 weeks showed no difference, indicating equilibrium was reached within a week. Previous ^{90}Sr aqueous-phase measurements indicated that equilibrium was likely reached within hours.

Results—Apatite-laden sediments. In contrast, the ^{90}Sr was more difficult to remove from the apatite-laden sediments. In the sediment in which ^{90}Sr was added to apatite-laden sediment, by 1 week only 50 percent of the ^{90}Sr was released by ion exchange, 31 percent by carbonate extraction, and 6 percent by residual extraction (Figure 3-7b). By 10 weeks, 42 percent of the ^{90}Sr could be extracted by ion exchange, 44 percent by carbonate extraction, and 12 percent by residual extraction. Therefore, the mass of ^{90}Sr bound by ion exchange is about one-half after 1 week, and continues to slowly decrease between 5 and 10 weeks, while the proportion of ^{90}Sr incorporated into carbonate and minerals increased. Additional experiments will be conducted in FY06 with Sr-laden apatite (no sediment) to determine the Sr extraction efficiency by EDTA and HNO_3 .

Results—100-N sediments with apatite added. For the 100-N sediment from the 13-foot depth (containing 80 pCi/g ^{90}Sr , no additional ^{90}Sr was added), addition of apatite also decreased ^{90}Sr mobility. At time zero (no apatite), 87 percent of the ^{90}Sr was extracted by ion exchange, 6.5 percent by the carbonate extraction, and 6.8 percent by the residual extraction (Figure 3-7a). These values were very similar to the sediment in which aqueous ^{90}Sr was added to untreated sediment (Figure 3-7a), indicating that the influence of approximately 40 years of aging was small. After 1 week of apatite addition, only 36 percent of the ^{90}Sr could be extracted by ion exchange, but 12 percent by carbonate extraction, and 23 percent by residual extraction. There were small changes over the next 10 weeks, indicating slow incorporation of ^{90}Sr into the apatite (Table 3-3). Therefore, the addition of the apatite decreased the ^{90}Sr mass on ion exchange sites by 59 percent in 1 week.

Table 3-3. Summary of ^{90}Sr Sequential Extraction Experiments

Untreated Sediment Apatite-Treated Sediment					
	Extraction	^{90}Sr (%)	Extraction	5 Weeks ^{90}Sr (%)	24 Weeks ^{90}Sr (%)
Mobile >	Aqueous	7.3	Aqueous	9.5 ↑	< 0.2 ↓
Slow Mobile >	Exchangeable	80.1	Exchangeable	44.5 ↓	34.6 ↓
Immobile >	0.05M EDTA	6.5	0.05M EDTA	48.5 ↑	49.7 ↑
Immobile >	4M HNO_3 , 80C	6.8	4M HNO_3 , 80C	7.0	17.2 ↑

Conclusion—The majority of ^{90}Sr in untreated 100-N soil is bound by ion exchange. However, in apatite-laden soil, only half of the ^{90}Sr was bound by ion exchange, and that slowly decreases over time. The addition of apatite decreases the ^{90}Sr mass on ion exchange sites by 59 percent in 1 week, with little change after 10 weeks.

3.2.4 Salt Effect: ^{90}Sr Desorption Associated with High Ionic Strength Reagents

As shown by the results presented previously, Sr is bound to sediment surfaces in the 100-N area primarily by ion exchange. In the presence of a higher ionic strength solution, some desorption of ^{90}Sr will occur. Apatite-forming chemicals, once injected into the aquifer, will contain higher salt concentrations than the groundwater in the treatment area. Some of these salts will not participate in the precipitation reactions, resulting in the migration of relatively high TDS water into areas where ^{90}Sr has not been sequestered by apatite, causing increases in pore water concentrations of ^{90}Sr .

To mitigate this problem, the apatite precursors will be introduced in steps. The first step involves injection of a dilute apatite solution that results in a minimal salt effect, but emplaces sufficient apatite to sequester the ^{90}Sr mobilized by the next injection. In the second step, a concentrated solution is introduced. Formation of apatite has been demonstrated at both high and low concentrations of apatite-forming chemicals.

PNNL conducted a series of experiments in FY05 to determine the influence of ionic strength on Sr adsorption. The purpose of these experiments was to measure the adsorption of Sr in natural Hanford groundwater and be able to predict how this adsorption may change with the injection of the apatite solution (Ca, Na, PO_4 , citrate).

Methods. Batch experiments were conducted with the 100-N composite sediment (less than 4 mm fraction) from well N-121 (depths 10 to 42 feet) with various Sr concentrations. Sr-85 was used as the isotopic tracer. The natural Sr adsorption was measured at two different Sr concentrations. The influence of ionic strength was tested with three different solutions:

1. Na_2SO_4 solutions
2. Fresh apatite solution (apatite-forming chemicals)
3. "Spent" apatite solution (5-week-old apatite solution)

In each case, Sr adsorption and electrical conductivity were measured to understand the correlation between K_d and the ionic strength of the apatite solution.

Results—Sr adsorption in natural groundwater. Three batch vials at two differing Sr concentrations (no apatite solution) showed that the Sr K_d value in natural groundwater is 25.96 ± 0.89 (Table 3-4).

Table 3-4. Sr Adsorption in 100-N Groundwater (less than 4 mm fraction)

Sr (mol/L)	Sr (mg/L)	Kd (cm ³ /g)	n	EC (μS/cm)
2.82E-07	0.0032	25.41±1.00	3	402
2.11E-06	0.024	26.51±0.26	3	365

Results—Sr adsorption in sodium sulfate solutions. Five different concentrations of sodium sulfate were mixed in 100-N groundwater to compare with the apatite solutions to determine if sodium concentration by itself was a good predictor of Sr adsorption. The Sr Kd decreased with increasing ionic strength (Table 3-5), as predicted, and were comparable to previously published results.

Table 3-5. Sr Adsorption in Groundwater + Na₂SO₄

Na (mol/L)	EC (uS/cm)	Kd (cm ³ /g)
0.001	508	20.89
0.005	952	21.2
0.01	1515	19.67
0.02	2560	18.46
0.03	3651	14.83

*all 2.11E-6 mol/L Sr

A Hanford 200 Area sediment in NaNO₃ solutions (Routson et al., 1981) had a Sr Kd value of 49 cm³/g (0.001 M NaNO₃), 42 cm³/g (0.015 M NaNO₃), and 16 cm³/g (0.1 M NaNO₃), so most of the Kd decrease occurred at ionic strength greater than 0.01 mol/L.

Results—Sr adsorption in fresh apatite solutions. Sr adsorption was measured in mixtures of fresh apatite solution and groundwater (2 percent to 100 percent). These results show a much more dramatic decrease in Sr Kd compared with the sodium sulfate, possibly due to aqueous Sr complexation with citrate (Table 3-6). These Kd values would be representative of Sr adsorption that would be expected in the first few weeks after an apatite injection. The Kd value decreased from 26 to 2.0 cm³/g as the ionic strength increased from 0.005 mol/L to 0.1 mol/L. In comparison, the same increase in NaNO₃ ionic strength (Routson et al., 1981) showed a four-fold decrease in Sr adsorption.

Table 3-6. Sr Adsorption in Groundwater + Fresh Ca/PO₄/Citrate

Na (mol/L)	% apatite solution	EC (uS/cm)	Kd (cm ³ /g)
0.35	100	24992	2.66
0.0875	25	8921	1.98
0.035	10	4123	6.47
0.0175	5	2220	13.1
0.007	2	1224	15.3

*all 2.11E-6 mol/L Sr

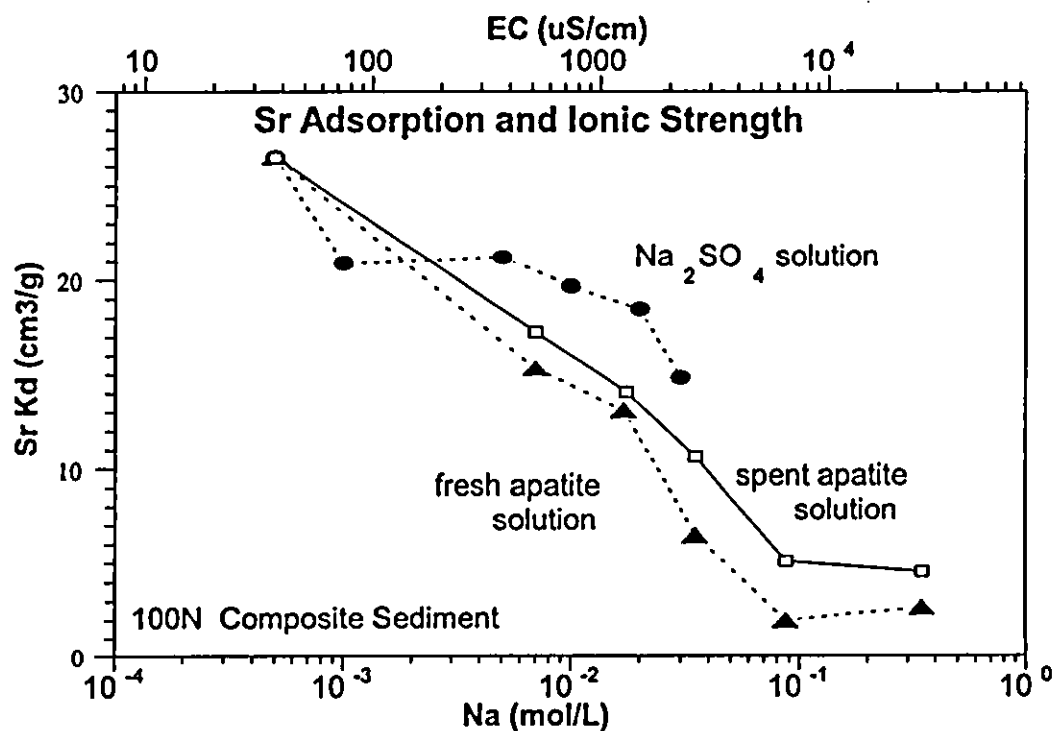
Results—Sr adsorption in spent apatite solutions. Sr adsorption in mixtures of a 5-week-old apatite solution and groundwater showed less influence on the Sr adsorption than the fresh apatite solution (Table 3-7). The Kd value decreased from 26 to 5.1 cm³/g (5.1x) as the ionic strength increased from 0.005 mol/L to 0.1 mol/L, which was similar to the change noted with NaNO₃ solutions (Routson et al., 1981). These experiments are representative of the solution that will be encountered downgradient of an apatite injection.

Table 3-7. Sr Adsorption in Groundwater + Spent Ca/PO₄/Citrate

Na (mol/L)	% apatite solution	EC (uS/cm)	Kd (cm ³ /g)
0.35	100	26337	4.53
0.0875	25	8596	5.1
0.035	10	3804	10.64
0.0175	5	2056	14.06
0.007	2	1089	17.26

*all 2.11E-6 mol/L Sr

Conclusion—The injection of an apatite solution will decrease adsorption of freshly adsorbed Sr from 26 cm³/g (in groundwater) to 4.5 cm³/g (spent apatite solution) or 2.7 cm³/g (fresh apatite solution) for 100 percent solutions. As groundwater dilutes the plume, there is less influence on the Sr adsorption, which shows a predictable trend of Na concentration (or electrical conductivity) in the apatite solution to the Sr Kd value. The sodium sulfate solutions generally follow the same trend, but do not accurately represent the trend observed with the apatite solution. Note that the two highest ionic strength points for the apatite solutions represent actual desorption Kd values (after 5 days of adsorption of ⁸⁵Sr), and as such represents a worst-case scenario. The influence of ⁹⁰Sr Kd is graphically shown in Figure 3-8.

Figure 3-8. Influence of Ionic Strength on ^{90}Sr Desorption (Ion Exchange)

3.3 Solution Concentrations and Injection Strategy

To lessen the ^{90}Sr release into solution caused by high ionic strength addition (i.e., the salt effect), injections will be staged, with an initial injection of lower apatite solution concentrations, which would also provide for more rapid citrate biodegradation (and ultimately better control of the apatite placement). With a 40 mM citrate injection, the $\text{Sr Kd} = 13 \text{ cm}^3/\text{g}$, which results in a two-fold increase in ^{90}Sr groundwater concentration. It is hypothesized that there would be less Sr desorption than predicted from these studies for actual ^{90}Sr -laden sediments that have been in contact with ^{90}Sr for decades (as opposed to the 5-day adsorption in this study). After several weeks of ^{90}Sr sequestration by the small amount of apatite, a high-concentration apatite solution can be injected.

Based on the above ionic strength ("salt effect") information, in order to keep most of the ^{90}Sr sorbed to the sediment surface (i.e., the ^{90}Sr groundwater increase kept to 2 to 3 times the ambient concentration), a low Ca/citrate/phosphate concentration needs to be injected initially to immobilize the ^{90}Sr in the immediate area. Because most of the final apatite barrier capacity is intended to sequester ^{90}Sr being advected into the precipitate zone, once the ^{90}Sr in the treatment zone (i.e., within 30 to 50 feet [9 to 15 meters] of the injection wells) is sequestered, new ^{90}Sr migrating into the treated zone will be adsorbed and then bound within the apatite structure. Subsequently, higher concentrations of Ca/citrate/phosphate can be injected and any initially desorbed ^{90}Sr will be trapped by the apatite formed by the low-concentration injections.

3.3.1 Injection Strategy

Based on the above considerations, an injection strategy is outlined as follows:

1. Begin with a low Ca/citrate/phosphate injection (5 to 15 mM citrate).
2. Allow a groundwater drift/apatite precipitation phase. This residence period is 3 to 7 weeks. Modeling of the citrate biodegradation experiments will determine the lag phase.
3. Inject high Ca/citrate/phosphate solutions (100 mM to 160 mM citrate) to build up mass of apatite to meet 300-year or alternate long-term objective.

Batch Tests

A series of batch experiments was conducted to test this injection strategy under idealized (laboratory) conditions. Results are reported as K_d values for Sr (^{90}Sr labeled Sr used), based on aqueous ^{90}Sr concentrations. With no treatment, the 100-N sediment (< 4 mm size fraction) has a $K_d(\text{Sr}) = 25 \text{ cm}^3/\text{g}$. Several different "low concentration" solutions were used in separate vials:

- The 2 mM apatite solution resulted in the $K_d(\text{Sr}) = 15.3 \text{ cm}^3/\text{g}$ (60 percent increase in ^{90}Sr groundwater concentration).
- The 5 mM apatite solution resulted in the $K_d(\text{Sr}) = 13.1 \text{ cm}^3/\text{g}$ (1.9x increase in ^{90}Sr groundwater concentration).
- The 10 mM apatite solution resulted in the $K_d(\text{Sr}) = 6.5 \text{ cm}^3/\text{g}$ (3.8x increase in ^{90}Sr groundwater concentration).
- The 25 mM apatite solution resulted in the $K_d(\text{Sr}) = 2 \text{ cm}^3/\text{g}$ (12.5x increase in ^{90}Sr groundwater concentration).

After 29 days, the apatite precipitated and because of some incorporation of ^{90}Sr into the apatite structure less ^{90}Sr remained in solution, so the ^{90}Sr K_d values changed to reflect this increase in solid-phase ^{90}Sr . The K_d values were:

- $23 \text{ cm}^3/\text{g}$ (2 mM citrate)
- $49 \text{ cm}^3/\text{g}$ (5 mM citrate)
- $61 \text{ cm}^3/\text{g}$ (10 mM citrate)
- $124 \text{ cm}^3/\text{g}$ (25 mM citrate)

The high ionic strength residual solution maintains some ^{90}Sr in solution in these batch vials, whereas in the field, the solution would be slowly diluted by downgradient advection.

To demonstrate that once ^{90}Sr is sequestered by the apatite a high ionic strength solution can be injected with little or no increase in the ^{90}Sr groundwater concentration, a 10 mM citrate solution was removed from the sediment and replaced with a 100 mM citrate solution. The resulting K_d value for ^{90}Sr was $340 \text{ cm}^3/\text{g}$. Apparently, ^{90}Sr is sequestered by the apatite and it is not desorbing into aqueous solution.

Column Studies

A series of column experiments are in progress to demonstrate the apatite injection strategy concepts, as described above in batch studies. Two column experiments were conducted to demonstrate Sr natural transport (i.e., high retention due to ion exchange). Both of these experiments (Figures 3-9a and 3-9b) consisted of 100-N sediment columns that were treated with Sr-85 (radio-labeled tracer) for 1 week, then 100-N groundwater was injected through the column for 150 to 350 pore volumes (pv) at a rate of 0.5 pv/h or 1.0 pv/h. In both cases, the resulting K_d was 12 to 13 cm³/g, or slightly lower than in the previous batch study ($K_d = 35$). There was some additional tailing observed at the faster flow rate (Figure 3-9b, tailing to 100 pv compared with 85 pv).

If a solution containing 100 mM citrate were injected into Sr-laden sediment, the Sr would desorb due to the high ionic strength of the injection solution, as described earlier in Figure 3-8. Ion exchange in a 1-D flow field will cause an initial peak, as illustrated in Figure 3-9c (100 mM citrate injection), in which the K_d of 2.04 (from area integration under the breakthrough curve) was the same as the batch experiment. This high amount of ⁹⁰Sr adsorption can be avoided by the sequential injection system consisting of: (1) 10 mM citrate injection, (2) allow a few months to incorporate ⁹⁰Sr into the apatite, and then (3) high 100 mM citrate injections.

A column experiment of the 10 mM citrate injection into ⁸⁵Sr laden sediment (Figure 3-9d) shows a small initial peak, but the Sr K_d decreased from 12 to 6.9 (i.e., only a 2x groundwater increase). At the field scale, this initial peak may be less a result of lateral dispersion (i.e., the column experiment represents the worst case results—similar to sampling a well at the downgradient edge of the injection plume). Additional columns are in progress to show: a) groundwater injection into ⁸⁵Sr /apatite-laden sediment, and b) 100 mM citrate injection into ⁸⁵Sr/apatite-laden sediment.

3.4 Summary of Bench Testing

Laboratory or bench studies have quantified the sequential processes of the aqueous injection apatite technology in 100-N sediment. The principal findings and results obtained to date are:

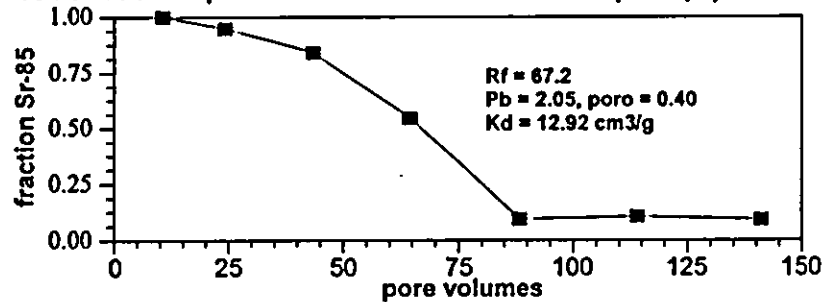
- Amorphous and crystalline apatite precipitation occurs.
- Aerobic and anaerobic citrate biodegradation pathways and rates were quantified.
- ⁹⁰Sr uptake in apatite-laden 100-N sediment occurs.
- ⁹⁰Sr is initially held by ion exchange, but then over 6 to 20 weeks is more permanently held (presumed incorporated into apatite).

Additional details of findings and laboratory work either underway or planned, and its relationship to field deployment, are discussed below.

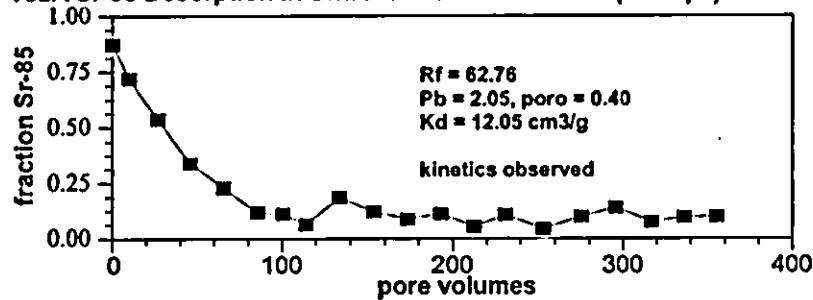
Apatite precipitation in batch and 1-D column systems occurred within 75-100 h in aerobic systems (100 mM citrate biodegrading to CO₂) and within 100-200 h in anaerobic systems (100 mM citrate biodegrading to formate and acetate).

Figure 3-9. Column Studies of ^{85}Sr Desorption from 100-N Sediments
a) and b) With Natural Groundwater Injection

T32 Sr-85 Desorption in Untreated 100N Sediment (1.0 h/pv)

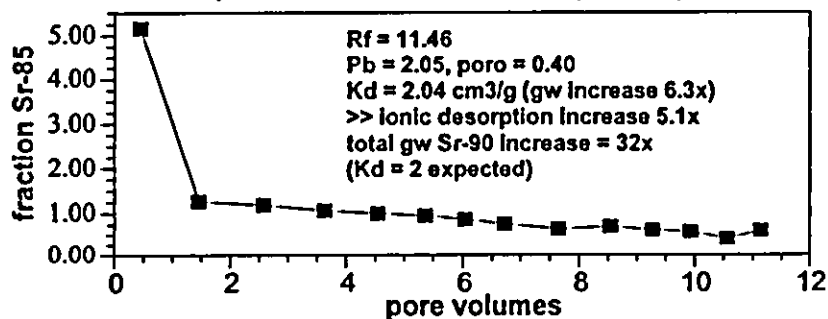


T32A Sr-85 Desorption in Untreated 100N Sediment (0.5 h/pv)



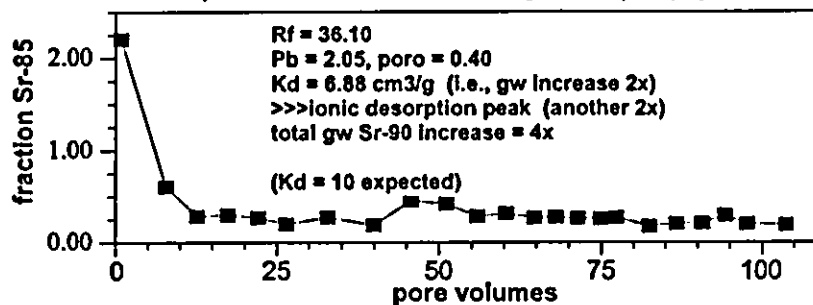
c) With 100 mM Citrate Injection

T33 Sr-85 Desorption with 100 mM Citrate Injection (1 h/pv)



d) With 10 mM Citrate Injection

T34 Sr-85 Desorption with 10 mM Citrate Injection (1 h/pv)



In the 100-N aquifer, most of the citrate biodegradation will occur anaerobically, given the relative concentrations of citrate to oxygen. The initial precipitate that forms within 100 h is amorphous and then crystallizes within 2 to 4 weeks to apatite. Batch experiments varying mixing, trace nutrient, and nitrate addition showed similar results. Apatite precipitate was formed in both batch tests and 100-N sediment columns. Precipitation experiments were conducted over a range of temperature and citrate concentrations to determine rates applicable to field-scale injection of 10 mM and 100 mM Ca/citrate/PO₄ at 15°C. Because microbial degradation of citrate occurs under either anaerobic or aerobic conditions, there will be no need to maintain the initial anaerobic response expected during field deployment. However, dissolved oxygen and or redox potential in pilot test monitoring wells during the field-scale test may be useful as an indication of microbial activity.

Performance testing of the apatite precipitate to sequester ⁹⁰Sr was accomplished with a variety of different experiments. Without apatite, sequential chemical extractions to remove ⁹⁰Sr from sediment showed that 90 percent of the ⁹⁰Sr could be removed from the sediment by ion exchange. With the addition of apatite, long-term experiments showed that by 6 weeks, only 45 percent of the ⁹⁰Sr could be removed by ion exchange, and this slowly decreased to 32 percent by 24 weeks. This may be caused by the slow ⁹⁰Sr incorporation into apatite.

To minimize ⁹⁰Sr mobilization (by ion exchange) during barrier emplacement, a sequence of injections from low to high concentration Ca-citrate/phosphate is needed. ⁹⁰Sr mobilization is minimal with the low concentration injection, and the apatite formed in the injection zone (after 4 weeks) immobilizes most of the ⁹⁰Sr, as demonstrated in a sequence of batch experiments and column experiments. A high concentration injection can then be injected with minimal ⁹⁰Sr desorption, as demonstrated in batch experiments. This finding is currently being confirmed in column studies. Additional laboratory studies quantifying ion exchange are needed to refine the design of field injections. Results of this effort, as available, will be used to update the initial injection conceptual design for the field testing described in Section 4.

Successful field-scale deployment will require injection of a sufficient volume of the Ca/citrate/PO₄ solution to achieve a relatively homogeneous precipitate over a specified lateral distance from the injection well. Laboratory-scale parameters needed to refine design of field injection strategies include:

1. Citrate biodegradation rates at appropriate temperature and concentration
2. Ion exchange parameters to predict spatial variability of Ca/Na/Sr during injections
3. Reagent adsorption

Techniques to test field performance include measurement of downgradient ⁹⁰Sr, measurement of apatite mass in field-treated cores, and measurement of ⁹⁰Sr ion exchange and/or leaching in field-treated cores.

Field pilot test data and injection simulations (Section 4) will be used to develop an initial injection strategy that incorporates reaction rates and parameters determined from the bench testing.

4.0 AQUEOUS INJECTION FIELD TESTING

The purpose of this treatability test is to determine whether introducing a solution of apatite precursors into the aquifer at the 100-N Area results in formation of apatite and subsequent reduction of ^{90}Sr concentrations in groundwater. This section provides a general description of the field-test design, performance assessment parameters, and general responsibilities.

4.1 Test Objectives and Conceptual Design

Field testing will consist of two phases: an initial pilot injection well test, followed by installation and treatment of a sufficient number of wells for a 300-foot (91-meter) treatability test barrier.

The objective of the pilot test phase is to address the following questions:

- Will apatite precipitate in the target zone?
- Does the apatite result in reducing ^{90}Sr in groundwater?
- Given a fixed well spacing of 30 feet, what is the optimal injection volume per well for installation of a 300-foot barrier wall?

Pilot testing will consist of a single injection well and associated monitoring wells installed at various radial distances. The proposed well layout design for the pilot test site is provided in Figure 4-1 (the actual configuration as staked and drilled may deviate somewhat from the general layout shown). Each of the five monitoring locations shown (numbered 1 through 5) will consist of a two-well set: one completed in the Hanford formation, and one in the Ringold formation.

A tracer test and/or low-concentration apatite injection will be conducted first to determine the radius and volume affected by injection at a single well point. If schedule constraints allow for performing a conservative tracer test prior to the low-concentration apatite injection, this information will be used in estimating the apatite-forming chemical solution volume, and concentration, to inject for a pilot test. Injection will be followed by performance assessment monitoring that may include a multi-pore volume withdrawal to force contaminated groundwater through the treatment zone.

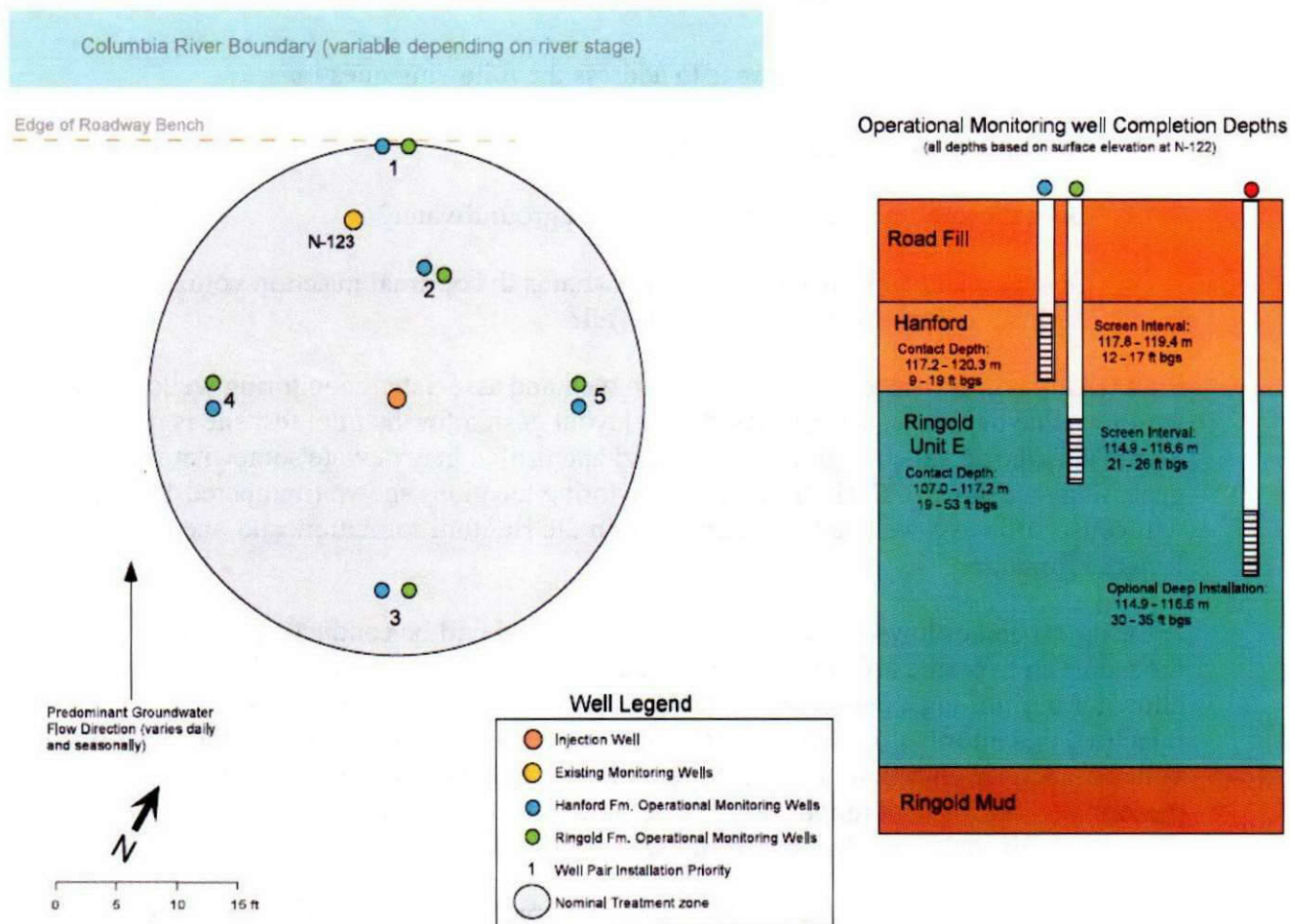
A detailed plan for the tracer and pilot testing is in preparation and will be available prior to the pilot test.

If the pilot test phase indicates that the aqueous injection approach meets performance objectives (Section 4.4.3) for the installation of an apatite barrier at the 100-N Area, the second phase of the treatability test will move forward with treatment of 10 injection wells for emplacement of a 300-foot PRB. Existing aquifer tubes near well N-46 and four compliance monitoring wells will be used to test the longer-term effectiveness of the barrier. Results of the pilot test will be used to determine the volume needed to obtain continuous

coverage across the 30-foot well spacing chosen for the 10 injection wells to be drilled (Section 5).

As discussed in Section 3, the concentration of calcium citrate and sodium phosphate for the initial injections will be maintained at concentrations low enough to minimize potential mobilization of ^{90}Sr that result from the salt leaching effect. Temporary release of ^{90}Sr from aquifer solids during subsequent injections at higher salt concentrations will be attenuated by the apatite in the formation from the initial low-concentration injections. Injection of the higher concentrations of apatite-forming solutions will be necessary to build up a sufficient load of apatite to treat ^{90}Sr for up to a 300-year period.

Figure 4-1. Pilot Test Site Well Layout

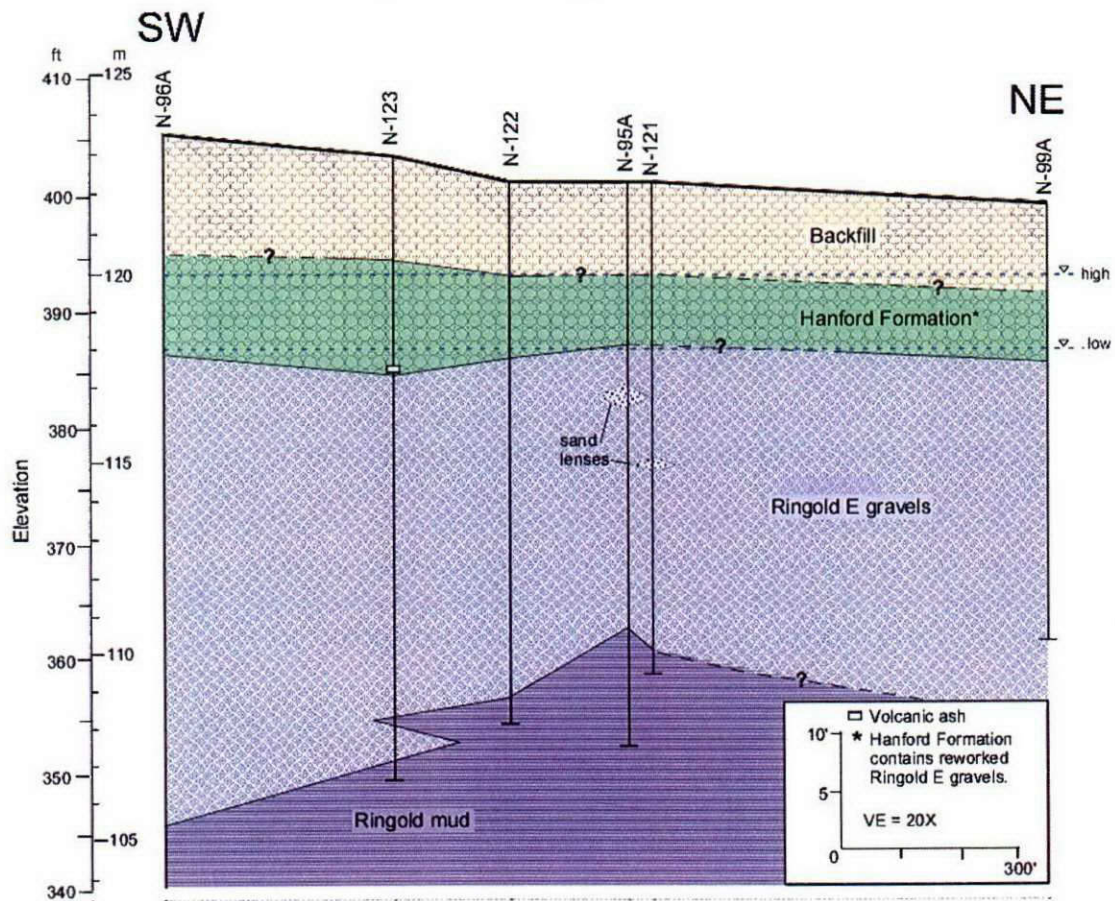


4.2 Site-specific Characterization

Two boreholes (N-122 and N-123) were drilled in FY05 to provide hydrogeologic and geochemical characterization data needed for the pilot test and overall barrier emplacement

design analysis. A geologic cross-section running along the proposed barrier alignment is provided in Figure 4-2. This cross-section was constructed based on hydrogeologic information obtained during the installation of the two new boreholes and from geologic logs from previous well installations. It should be noted that the zone designated as the Hanford formation contains a significant amount of reworked Ringold formation materials, with this effect more evident at the N-123 location. Both of the boreholes were completed as downgradient performance assessment monitoring wells. As the boreholes were advanced, continuous core samples were collected and submitted for grain-size analysis, microbial characterization, and determination of ^{90}Sr concentration with depth. These data will be used to determine the depth interval for initial treatment and will decrease uncertainty associated with the depth to the Hanford/Ringold contact and the vertical distribution of ^{90}Sr in the proposed target area where clam tissue data indicate the highest impact.

Figure 4-2. Geologic Cross-Section



Because of the large difference in aquifer permeability between the Hanford and Ringold formations, determining the primary formation requiring treatment is essential to the injection design. If treatment is required in both the Hanford and Ringold formations, the two formations would need to be treated independently. Electromagnetic borehole flowmeter (EBF) testing will be conducted at the site to help quantify the permeability of each formation and determine the contact depth. The hydrogeologic and geochemical characterization data collected from this site will be the basis for a flow and reactive transport model. This design tool will be used to develop the design for the pilot study as well as for the final barrier.

4.3 Flow and Reactive Transport Simulations

The injection design analysis will be used to develop a strategy for injecting the apatite-forming reagents. This approach will target a depth interval of the unconfined aquifer as determined from the results of ^{90}Sr vertical profiling described previously (see Section 4.2) and from prior ^{90}Sr vertical profiles.

There are two potential zones of treatment: 1) Ringold formation E Gravels (lower contaminated portion of the unconfined aquifer), and 2) Hanford formation (upper contaminated portion of the unconfined aquifer). The permeability of the Hanford formation gravels can be 10 to 1,000 times greater than the permeability of the Ringold formation gravels. The material properties of these units will impact the injection rates and volumes, extent of injection mounding, extent of reagent plume, ambient groundwater velocities (e.g., plume drift after injection period), and density effects.

The pilot test design will provide specifications of the injection and monitoring wells, injection rate, injection volume, reaction period duration, withdrawal rate for multi-pore volume performance assessment extraction test, and the sampling/analysis plan. The timing of the injection relative to the river stage regime is also a critical factor for treating the targeted portion of the aquifer because of the strong influence of the river stage on the water table elevation and the groundwater flow directions and velocities. The river stage is very dynamic with large hourly, daily, weekly and seasonal variations.

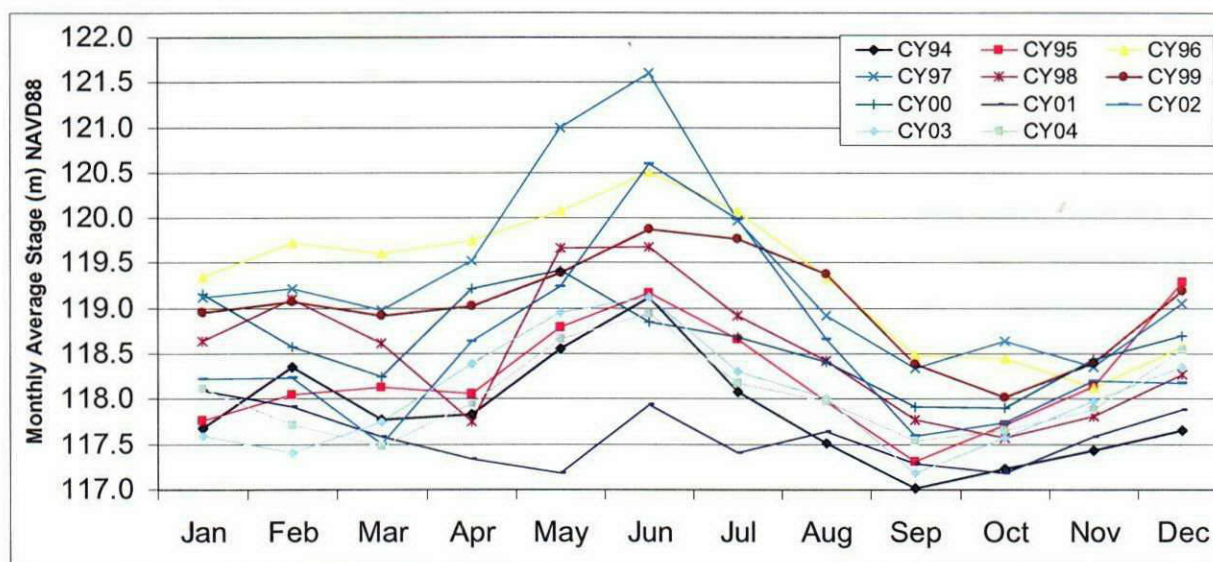
Although the timing and extent of the large seasonal variations in the Columbia River stage changes from year to year depending on weather and dam operations, hourly measurements from the RS-1 river stage recorder at the 100-N Area for the years 1994 through 2004 show a high river stage season typically from April to June and a low river stage season typically from August to November (Figure 4-3). During seasonal high conditions, groundwater flow is predominantly directed inland at distances approximately 40 meters (131 feet) from the river (simulation results discussed below). During seasonal low conditions, larger groundwater velocities are directed toward the river.

The timing of the injection test relative to the Columbia River stage will also control the portion of the aquifer that can be treated. This may be an important factor based on previous studies showing that the highest ^{90}Sr concentrations in the sediment are in the upper portions of the aquifer or slightly above the mean water table. Injections during periods of relatively high river stage will enable treatment of this portion of the aquifer.

Following the reagent injection, from 70 to 200 hours is required for apatite precipitation based on bench-scale laboratory studies. During this period, the injected reagent plume will drift with the ambient groundwater flow. The timing of the pilot-scale test relative to the river stage will be important in determining the direction and amount of plume drift that will occur during this phase of the test, which in turn will determine where the apatite precipitate will form.

Figure 4-3. Monthly Average River Stage at N-Area from RS-1 for 1994 to 2004

*Averages were calculated from hourly measurements; elevations are
NAVD 1988 Datum 100-NR-2 Operable Unit*



With the immediate proximity of the pilot-scale test to the Columbia River, the potential exists for reagent and reaction products to enter the river. This is particularly true for treatment of the Hanford formation (with its high groundwater velocities) at low river stage when the velocities are directed toward the river. Heterogeneities in the formations can also create highly conductive channels toward the river. Site-specific tracer tests and simulations will be used to provide guidance on the extent and relative concentrations of reagent that could enter the river during the treatment phase.

Numerical simulations will be used initially to aid in the design of the pilot-scale test (e.g., injection volume and rate). These models will be refined as additional site-specific characterization data become available from additional boreholes and tracer tests conducted at the site. If the pilot-scale test is successful, results will be used to update the models and aid in the design of the large-scale implementation (e.g., injection volumes and rates, timing of injections relative to river conditions).

4.3.1 Previous Modeling Studies

As part of the 100-N Area ITRD Program, detailed groundwater modeling studies were conducted with a calibrated, transient, two-dimensional cross-section model using hourly measurements of water levels in wells and the river stage from 1995 (Connelly et al. 1997,

Connelly 1999, and Connelly 2001). The results of these simulations and the animations developed along with them illustrate the dynamic behavior of the groundwater flow at the site that is driven by the fluctuating river stage. The modeling study found “flow velocities in excess of 20 m/day were often predicted for the Hanford formation, while the highest velocities predicted in the Ringold formation were approximately 1 – 2 m/day” (Connelly, 1999, p. 33). Animations of the simulation results showed the higher velocities within the aquifer occurring closer to the river particularly during the low river stage season.

4.3.2 Simulations for Designing the Pilot-Scale Test

Initial simulations for designing the pilot-scale test used the 100-N Area cross-section model developed for the ITRD project discussed above (Connelly et al., 1997; Connelly, 1999; and Connelly, 2001), and used the STOMP computer code, which was developed by PNNL for simulating subsurface flow and transport in the aquifer and vadose zone (White and Oostrom, 2004; 2003; Nichols et al., 1997). The STOMP code will also be used for other design analyses. Material properties for these models will use the values developed for the calibrated ITRD Model (hydraulic conductivity, porosity, dispersivity, and soil characteristics) shown in Table 3-2 of Connelly (1999). These parameters will be updated as additional characterization data become available.

The following list outlines the models that will be developed and used in the design analysis for the pilot-scale test:

- Two-Dimensional Cross-section Model (ITRD model or a revised cross-section model if geology for specific site does not match the ITRD cross-section). The purpose of this model will be to investigate groundwater flow velocities at different locations and the drift of instantaneous plumes at different periods of the year/river stage regimes.
- Three-Dimensional Model. This model will be used for simulating the plume formation during injection and plume drift following the injection of the pilot-scale test and will provide for a fluctuating river boundary and an inland held head boundary. These simulations will be run at different times of the year with different river stages.
- Two-Dimensional Radial Model (may not need if the resolution of the three-dimensional model is adequate). This model will be used for simulating near-well effects during injection.

To support the construction of the three-dimensional model and other two-dimensional model cross-sections, an EarthVision GIS database of the Hanford Site was refined and updated for the 100-N Area based on detailed well logs and additional wells. This process identified some facies within the Hanford and Ringold formations (see Figures 4-4 and 4-5 for a transect location map and a geologic cross-section through the ITRD model transect location, respectively). The EarthVision hydrostratigraphy will be sampled at finite difference STOMP model node locations to determine the hydrostratigraphic unit for each node. One past limitation has been that the topographic data were insufficient to resolve the

road and bank near the river at N-springs. A new topographic survey was conducted by PNNL in September 2005 that provided detailed elevations around the proposed pilot-scale test site.

Simulations will be conducted to investigate the impacts on the reagent plume extent and drift by potential heterogeneities and by fluid density from the injected reagent. Simulations will be conducted using both the low-concentration and the full-concentration injection fluid densities.

Conservative tracer and reactive transport simulations will also be conducted to predict apatite precipitation within the aquifer under varying conditions. To test the models used, reaction mechanisms and rates from bench testing laboratory studies will be compared to results from simulated bench tests. The reaction rates for the field test simulations will be suitable for ambient aquifer temperatures measured at the pilot-scale site.

Figure 4-4. Plan View Map Showing Locations of EarthVision Cross-sections
100-NR-2 Operable Unit

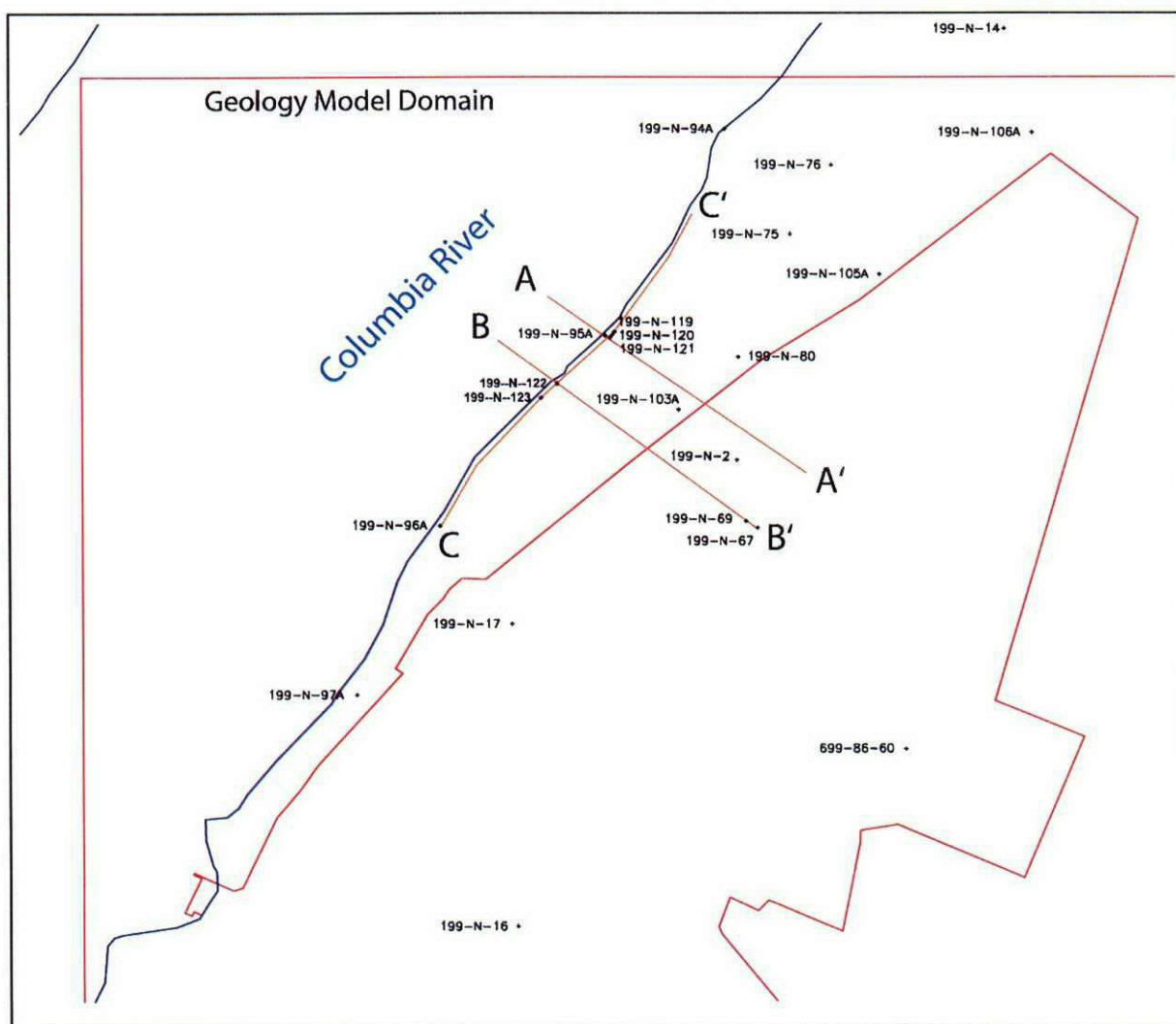
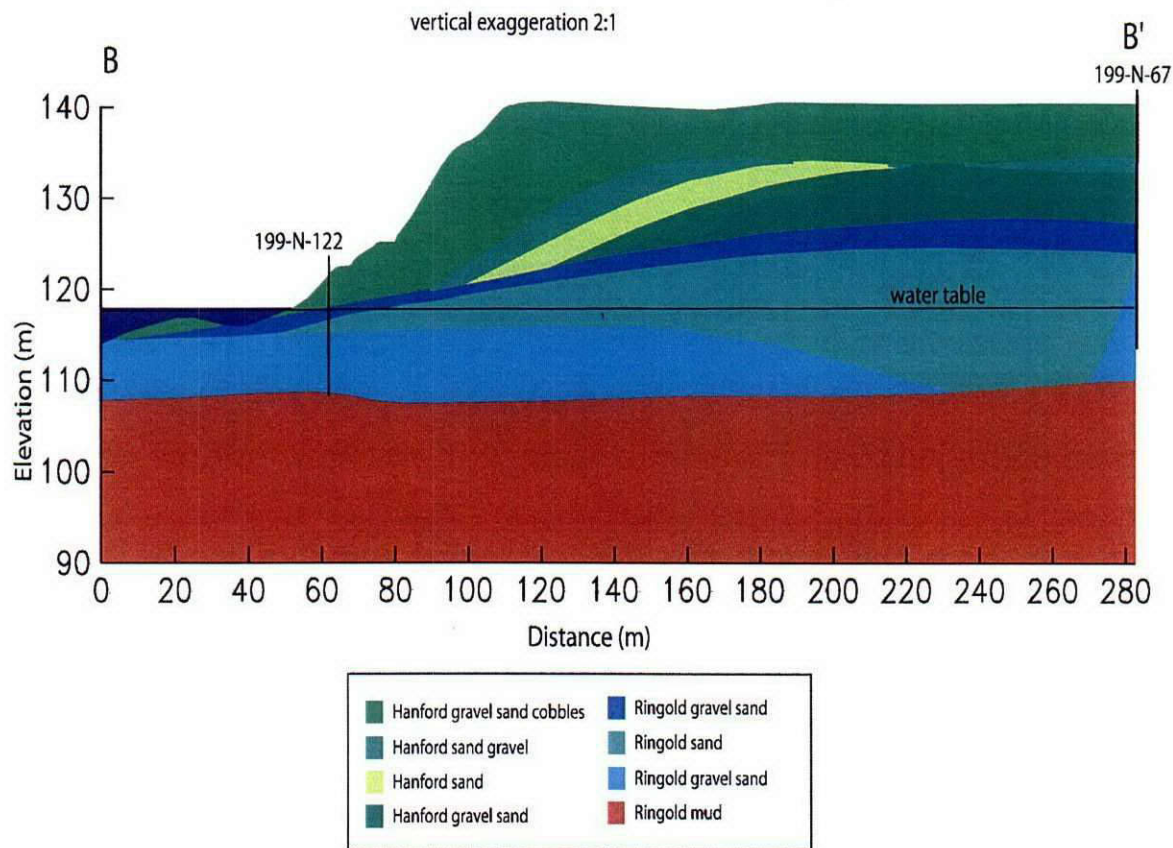


Figure 4-5. B-B' Cross-Section

Elevation in NAVD88 Vertical Datum 100-NR-2 Operable Unit

Prior injection tests conducted at the Hanford site have demonstrated the impact of heterogeneities on the extent, coverage, and shape of the reagent plume formed. A limited number of simulations will be conducted with heterogeneous hydraulic conductivity distributions to investigate the potential impact on the plume formation and drift. While site-specific data on heterogeneities at the proposed pilot-scale site may not be available, data collected at the other sites at Hanford will be used to generate stochastic realizations for the Hanford and Ringold units (e.g., EBF data collected in the Ringold formation E Gravels at 100-D Area In Situ Redox Manipulation [ISRM] site). A conservative tracer test conducted at the site will provide the best information on the impact of heterogeneities on the plume formation and drift.

4.3.3 Tracer Simulations

Preliminary simulations were conducted using a two-dimensional cross-section model along the transect shown in Figure 4-5, to help understand the amount of plume drift that could be expected during different periods of the year near the river at 100-N Area. These simulations are similar to those developed by Connelly et al. (1997; 1999; 2001) and used the same material properties; however, the geology and topography were updated based on field work conducted in FY05 (i.e., topographic survey and additional wells installed). Tracer pulses

were created at midnight during high and low river stage periods in 1995. The tracer pulses were created by specifying a solute source over the Hanford and Ringold formations to create a unit concentration for an approximately 5-meter (16-foot) width. The initial tracer plumes were created near the center of the road in the cross-section between well N-46 and the Columbia River. These tracer pulses were created almost instantaneously and were not simulating well injection (e.g., no fluid sources). Following the tracer pulse release, simulation results were output hourly and daily for 10 days to illustrate the plume drift with the ambient groundwater flow as it fluctuates with river stage.

Figure 4-3 shows the calculated monthly averages of the 100-N Area river stage for the years 1994 through 2004. Typically, the highest monthly average is during the spring, with the lowest in September. 1995 was not a typical year because the December monthly average river stage was slightly greater than the June average stage.

Figures 4-6 and 4-7 show the results of a tracer pulse in the Hanford and Ringold formations during the highest (late June) river stage period in 1995 (Figure 4-6). The resulting movement of the tracer plume over this 10-day drift is shown in Figure 4-7. Simulation results show the tracer moved a significant distance away from the river in the Hanford formation during this period, with relatively little movement in the Ringold formation. Animations of the plume movement in the Hanford formation showed that the daily changes in river stage had a large impact on the drift, with plumes moving toward and then away from the river as the river stage shifted. It is important to note that the river stage was relatively low for a few days prior to this tracer pulse (see Figure 4-6), which would yield steep hydraulic gradients initially. These simulations also show some tracer in the vadose zone above the water table as a result of simulated fluctuations of the water table. Although the tracer concentrations may remain high in the soil moisture within the vadose zone, the overall tracer mass in the zone would be low because of the low moisture content.

Figures 4-8 and 4-9 show the results of a tracer pulse in the Hanford and Ringold formations during the lowest (early September) river stage period in 1995. The timing of this tracer pulse occurred after a long period of much greater river stages at the end of August (Figure 4-8). At the beginning of this period, there was a thin layer of saturated Hanford formation, but by the end of this period the water table had dropped into the Ringold formation (Figure 4-9). As the water table lowered, there was substantial movement of the tracer toward the river in the Ringold formation because of the steeper hydraulic gradients in that formation. During the high river stage period (Figure 4-7), not much movement was seen in the Ringold formation because the water table was mostly in the much more permeable Hanford formation during that pulse.

While these simulations demonstrate the dynamic nature of plumes near the river at the 100-N Area, a number of limitations and assumptions in this model could still be under-predicting the extent of spread and variability in the plume geometry expected in the field. These factors include heterogeneities (the model assumes homogeneous Hanford and Ringold formations), density effects, and field-scale porosity (site-specific values are needed and may be lower than the values used in the model). Actual tracer tests conducted at the proposed test site would help in further understanding the plume behavior. The general river stage during the creation and reaction period of the plume is important in determining vertically where the

treatment zone will be created (e.g., generally high river stage is needed to treat the zone above the average water table). Additionally, these simulations show the importance of the relative daily changes in river stage over the reaction period of a plume on the direction, extent, and distribution of reagent.

Figure 4-6. 100-N Area River Stage for the First Half of 1995 Showing Timing of 10-day High River Stage Tracer Pulse (see Figure 4-7). Bottom Plot Shows Detailed View.

100-NR-2 Operable Unit

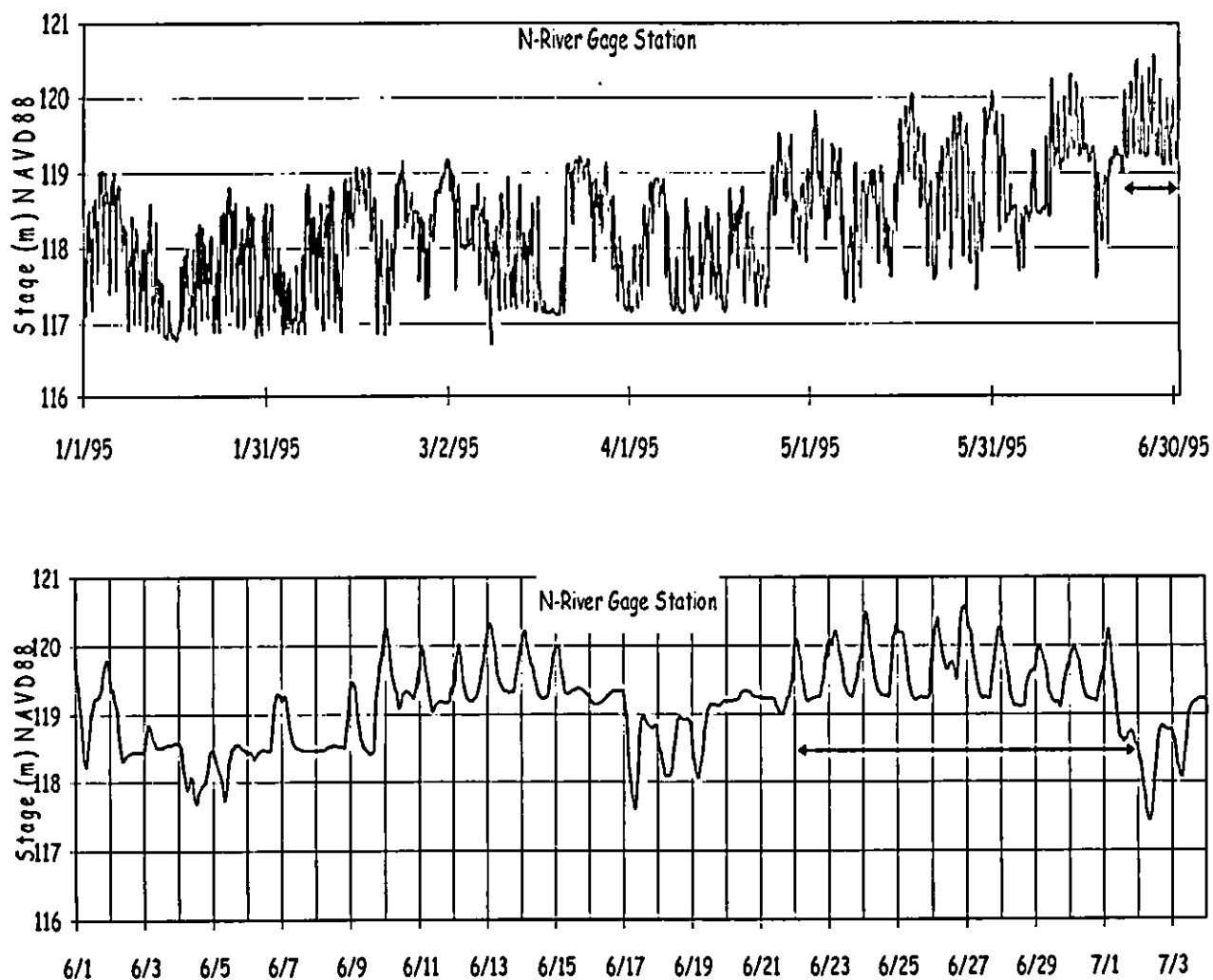


Figure 4-7. Simulated Tracer Concentrations in Hanford and Ringold Formations During a High River Stage Period
(June 22 to July 1, 1995 – see Figure 4.6 For River Stage During This Period)

View along cross-section centered on road. Results are shown at the start of pulse, 1 day after pulse, 5 days after pulse, and 10 days after pulse. Black line shows the water table. Green line shows the Hanford/Ringold contact. Elevations are NAVD 1988 Datum.

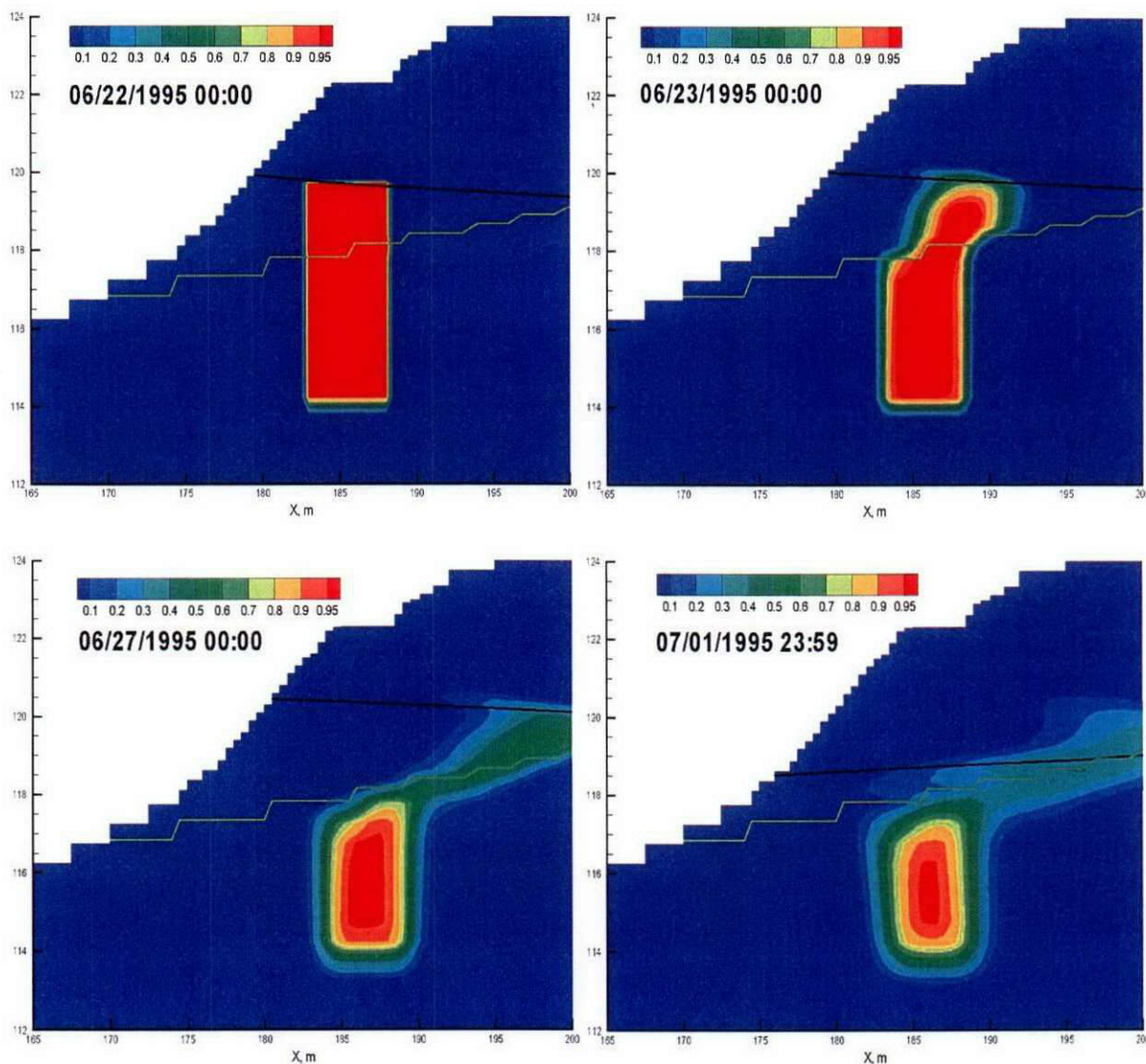


Figure 4-8. 100-N Area River Stage for the Second Half of 1995 Showing Timing of 10-Day Low River Stage Tracer Pulse (see Figure 4.9). Bottom Plot Shows Detailed View.

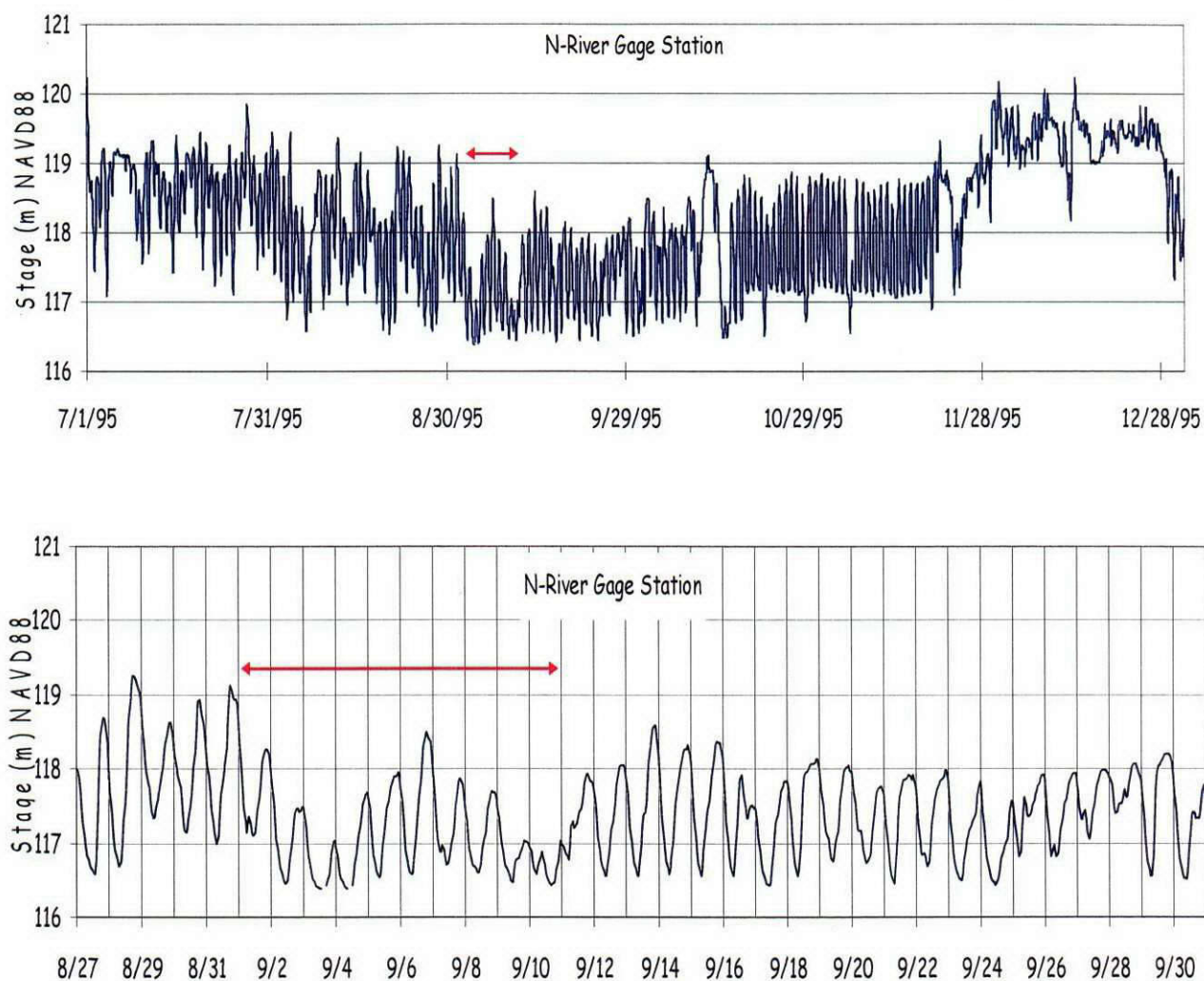
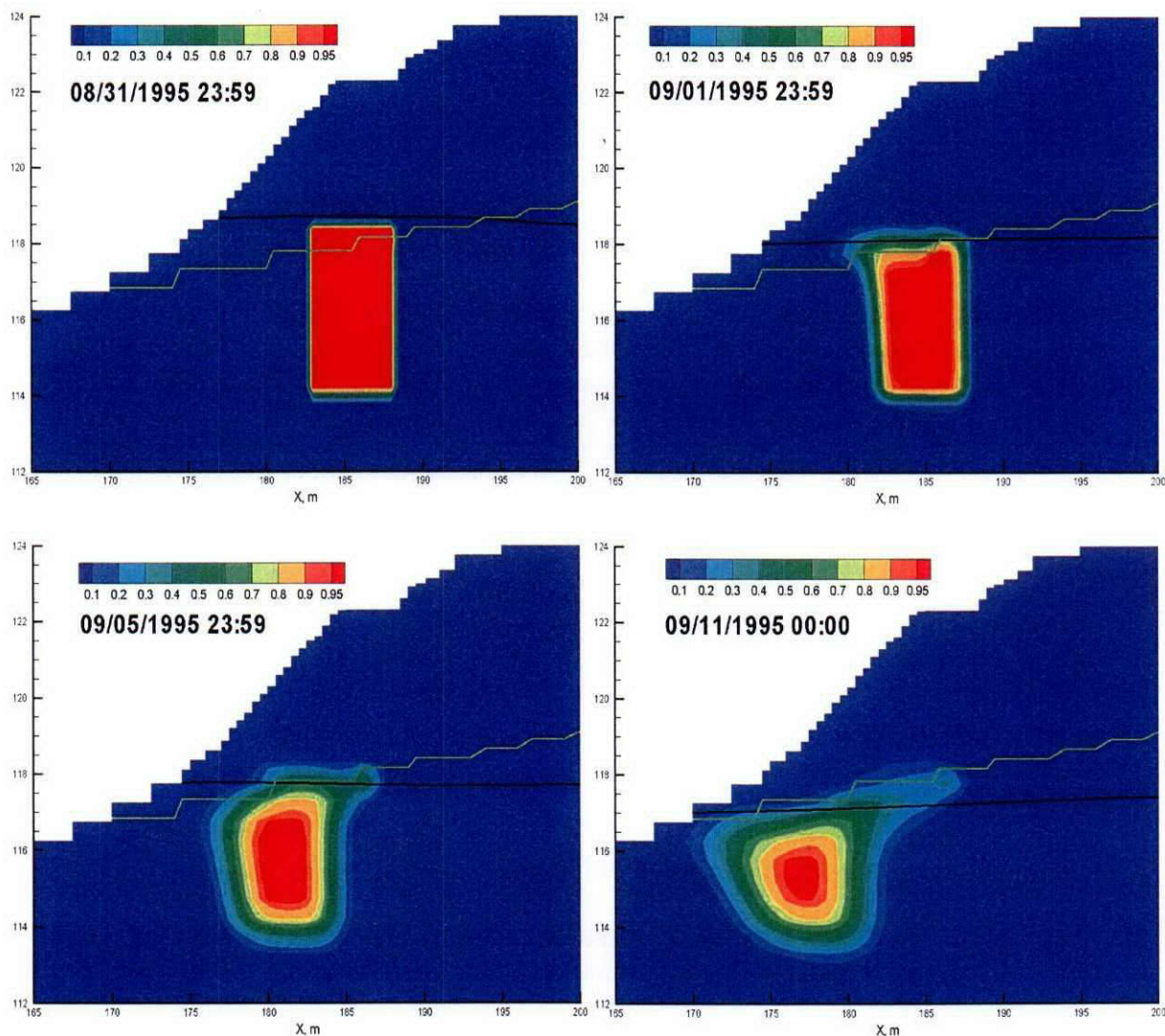


Figure 4-9. Simulated Tracer Concentrations During a Low River Stage Period (September 1 to September 10, 1995 – see Figure 4.8 for River Stage During This Period).

View along cross-section centered on road. Results are shown at the start of pulse, 1 day after pulse, 5 days after pulse, and 10 days after pulse. Black line shows the water table. Green line shows the Hanford/Ringold contact. Elevations are NAVD 1988 Datum.



4.4 Field Test Specifications

This section provides the basis, specifications, and responsibilities for preparation of supporting work plans and documents to implement the planned testing activities. A general schedule of major activities is included in Section 5.

4.4.1 Field Test Location

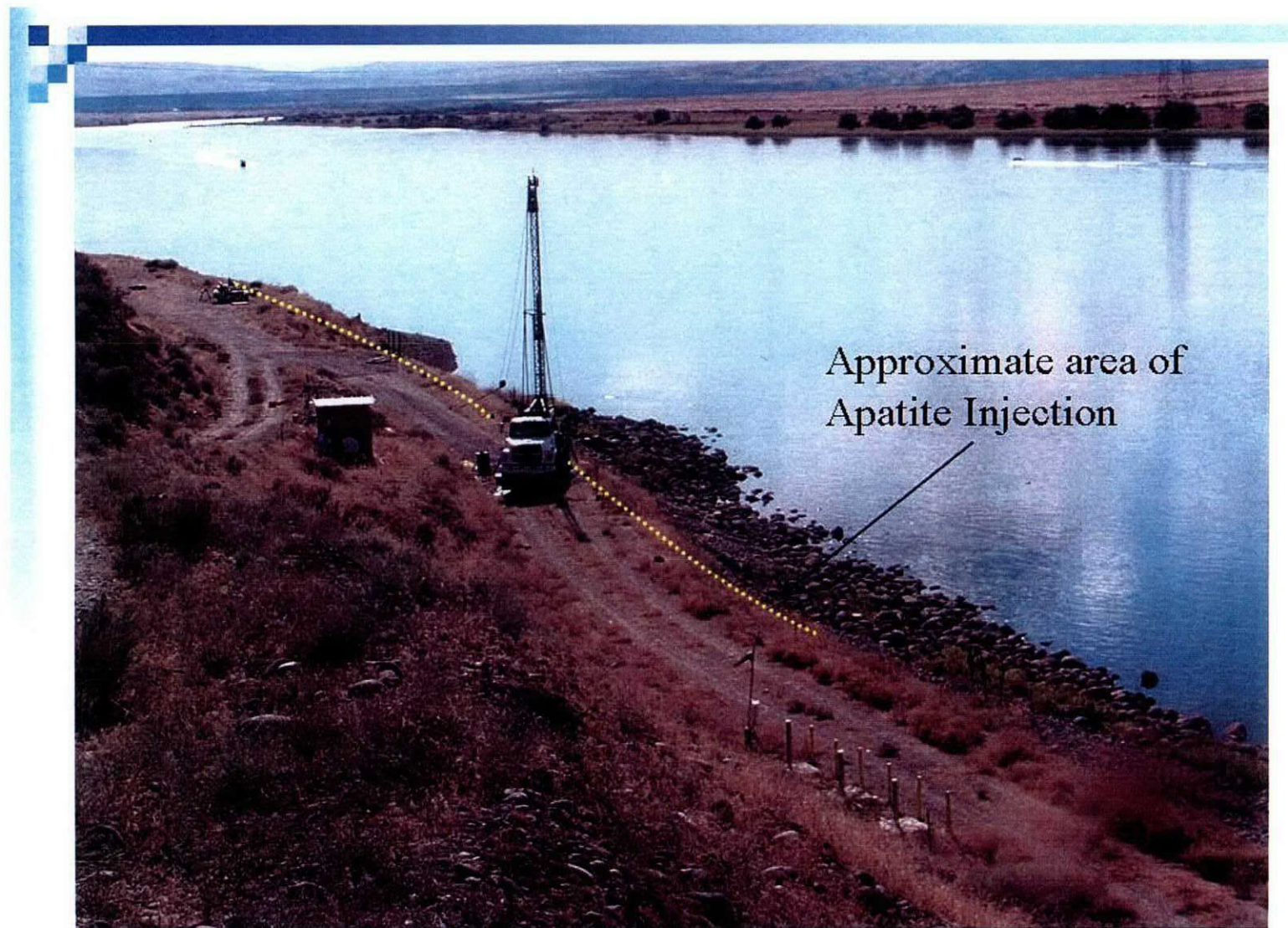
The pilot test injection well, and the injection wells for the 300-foot barrier, will be located within the section of the shoreline where the highest ^{90}Sr concentrations have been observed in clam tissue and aquifer tubes (see photo, Figure 4-10). Based on the characterization data discussed in Section 4.2, a pilot test site will be conducted within the planned barrier location. The site will be located within the reach showing elevated ^{90}Sr concentrations but may not necessarily be located at the location of maximum observed concentration, because of space limitations for layout of the pilot scale test well array.

Access to the construction zone will be provided along the existing ramp and gravel access road near the Columbia River. Construction activities will be limited by the width of the bench, which in some areas is only 15 feet. It is assumed that no modification will be needed to permit truck and equipment access to the construction area. PNNL will perform the initial pilot test of the technology with field site logistical support (i.e., electrical service or generators, waste handling, site access, etc.) provided by Fluor Hanford. Upon successful completion of the pilot test and subsequent development of the PRB emplacement design, PNNL will transfer the technology to Fluor Hanford for full-scale deployment. Injection equipment and field support trailers from the 100-D Area ISRM site will be used to conduct the injections for emplacement of the 300-foot barrier. (Success for the pilot test will be based on indications that the apatite formed under field conditions as expected based on bench scale results; that is, significant decline in citrate concentration due to microbial activity and reduction in ^{90}Sr concentrations in water samples removed from the test well array).

Following are the site-selection criteria that were used to select the proposed site. These same criteria will be used to guide selection of the final pilot test site location.

- **High ^{90}Sr Contamination** – The site location was chosen because it was identified as the area of greatest ^{90}Sr contamination along the river at the 100-N Area, as discussed in Section 1.
- **Test Site Accessibility** – The site location is accessible by the heavy equipment needed to install the PRB and monitoring wells, allowing sufficient space for material delivery and staging upstream of the proposed barrier wall.
- **No Disturbance, or Minimal Disturbance, of Culturally Sensitive Areas** – The site location is in a previously disturbed area along the Columbia River shore, and natural bank and floodplain areas will be minimally disturbed. No known cultural resource sites should be affected.

Figure 4-10



- **Adjacent to Existing Monitoring Wells** – Locating the pilot test injection point in immediate proximity to existing monitoring wells, and or aquifer tubes, provides the potential to reduce cost and/or provide more testing data. It is possible that an existing well can be used to replace one of the new test wells in the scope of this test, or can be used to collect additional data to supplement that gathered from new monitoring wells. Installation will be located to minimize potential impact to existing wells or monitoring wells.
- **Sufficient Area for Construction** – There is sufficient area at the selected site to accommodate the following:
 - Minimize risk of exposure to workers and environment (e.g., sufficient area for the establishment of a controlled contaminated area to allow for the safe loading and transport associated with the construction)
 - Provide for development of a safe construction zone throughout the entire area required for PRB and monitoring well installation and access for construction equipment
 - Sufficient area for staging of equipment and materials
 - Retain ability to use access road after injection well installations

4.4.2 Test Well Specifications

Well locations and design specifications will be developed based on site-specific characterization data and results from the design analysis discussed previously. As dictated by cost and technical requirements, injection wells will be constructed using either 4-inch or 6-inch-diameter casing and screen and monitoring wells will be constructed using either 1-inch, 2-inch, or 4-inch-diameter casing and screen. It is anticipated that the pilot test will require one injection well and five monitoring well pairs (Hanford and Ringold completions). In addition, nine additional injection wells will be required to emplace the remainder of the 300-foot PRB. Up to four additional operational monitoring wells will be installed at intervals along the barrier to provide a measure of consistency in emplacement operations along the full length of the barrier.

4.4.3 Field Test Performance Assessment

The pilot test will be considered successful if post-emplacement performance assessment testing indicates favorable results described as follows. After an approximately 3-week residence period (i.e., approximately 1 week for formation of amorphous apatite and another 2 or more weeks for conversion to the crystalline form), water will be extracted from the injection well. The extraction rate and volume will be based on results from the design analysis and will be selected to remove the desired volume of groundwater in as short a time as possible without exceeding ^{90}Sr adsorption kinetics. ^{90}Sr concentrations and associated chemical parameters (e.g., major anions and cations, electrical conductivity, pH, temperature) will be measured in the purged water. If ^{90}Sr concentrations in purge water are reduced by

tenfold, the proof of principle will be demonstrated. Alternatively, if disposal of a large volume of purge water is not feasible or practical, samples from the pilot test monitoring array will be used to determine the reduction in ^{90}Sr concentration in the treated zone around the injection well. After consultation and agreement between DOE and Ecology, a decision will be made to proceed with the next phase of the testing. Results from the pilot test will be used to prepare a final deployment field installation plan to complete the treatability test.

The 300-foot low concentration PRB test will be considered successful if the following conditions are met:

- ^{90}Sr is removed from groundwater in the treatment zone (i.e., >90 percent reduction in ^{90}Sr concentrations in water samples withdrawn from pilot test and performance monitoring wells and/or injection wells).
- There is minimal impact on Columbia River water quality or aquatic habitat
 - Impacts from injected reagents will be evaluated during the pilot test and results provided to DOE and Ecology for their concurrence to proceed with the planned injections for the 300-foot test barrier
 - Aquifer tube monitoring at the shoreline will be conducted during the pilot test and 300-foot barrier test to assess chemical impacts
 - A monitoring plan for the above purposes will be included in the pilot test field instruction and provided to Ecology for review prior to the pilot test

Damage control measures will include the following:

- The planned 2006 treatability testing will begin with low concentration (0.01 molar) chemical solutions in order to minimize potential water quality impacts
- Protective berms and runoff controls will be located as necessary to prevent sediment transport to the river
- An area will be demarcated specifically for the temporary storage of contaminated soil and groundwater
- A lined decontamination (decon) pad will be constructed for containment of contaminated material removed from equipment.

Assuming the low concentration PRB test is successful (as defined above), high-concentration injections, to establish sufficient apatite for long-term treatment, will be conducted in 2007 or 2008. Core sampling and associated laboratory testing will be conducted after the final injections to assess the mass distribution of in situ apatite and to evaluate barrier longevity (an addendum to this TTP will be issued for the high-concentration injection phase).

4.4.4 Water Quality Impact Evaluation

FY2006. As indicated above, the treatability testing planned for FY06 is limited to dilute chemical solutions (0.01 molar) because of the concern that the higher concentrations (~0.1 molar) originally proposed could result in adverse impacts on shoreline water quality and benthic biota. Potential adverse impacts include displacement of toxic metals from the sediments by the salt residue from the apatite-forming chemicals, and adverse effects from depressed dissolved oxygen or elevated salt content.

Because of the concern that a limited “die-off” of shoreline biota (e.g., benthic invertebrates and periphyton) may result from injection of higher concentrations, a dilute solution, single injection well pilot test will be conducted to evaluate potential water quality impacts that might occur at a larger scale and with higher loadings. Results from this test will be used to plan follow-on work.

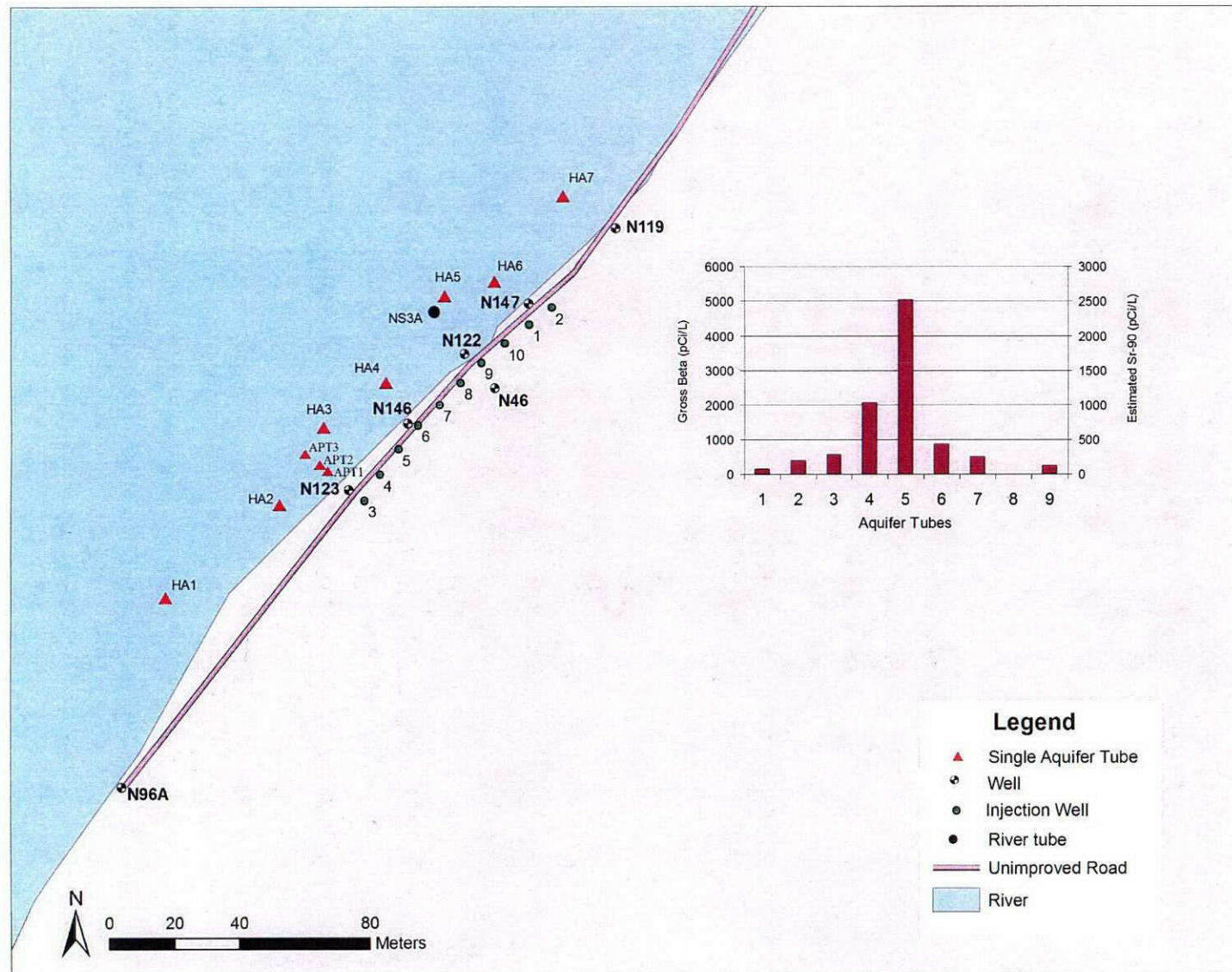
To confirm the expectation that minimal impacts will result from the planned treatability test, water samples will be collected from 11 observation wells within a 6-meter radius of a single injection well (IW-3; see Figures 4-1 and 5-3) during the pilot scale injection test. Water samples will be analyzed for inductively coupled plasma (ICP) metals (Fe, Mn, Pb, Cd, etc.) and water quality indicators (specific conductance, pH, dissolved oxygen). This information, combined with predictions of mixing and dilution of the transient chemical plume in the streambank storage zone just prior to emergence in riverbed gravels, will be compared to surface water quality standards (WAC 173-201A with appropriate allowance for mixing zones and acute conditions or short-term modifications), and provided to Ecology to support the decision to proceed (or not to proceed) with the 300-foot treatability test injections (10 wells).

Water quality monitoring for the planned 300-foot barrier emplacement will involve sampling existing aquifer tubes at the shoreline and performance monitoring wells located immediately adjacent to the injection wells (Figure 4-11). Potential impacts will be tracked using the aquifer tubes and performance monitoring wells shown in Figure 4-11. These wells are, or will be, included in the PNNL Hanford Site groundwater monitoring project master schedule (PNNL 15070, Table A.5, Appendix A). A baseline water level and constituent monitoring effort was initiated in 2004 in anticipation of the pump-and-treat shutdown and treatability test. The existing sampling frequency and constituents of interest will be supplemented as necessary to accommodate the injection and first year post-injection period. A supplemental monitoring plan for this purpose will be provided to Ecology for review.

During injections, more frequent monitoring in the adjacent performance wells (N-122, N-123, N-146, and N-147) will be performed to track the arrival of treatment chemicals and or changes in water quality. At least one of these wells (N-146) will be equipped to continuously record water level, specific conductance, and dissolved oxygen during the injections and for an appropriate post-injection observation period.

FY2007-2008. If the pilot test using dilute apatite-forming chemicals meets both the ^{90}Sr sequestration and minimal adverse water quality impact objectives, efforts will focus on increasing the mass of in situ apatite to address the long-term sequestration issue, including

allowance for other competing cations. This will most likely involve the use of higher concentrations of treatment chemicals. If so, additional water quality impact evaluations will be made. This may involve aquarium-scale biological testing to evaluate the potential effect of the higher concentrations of un-reacted citrate and phosphate solutions and mobilized metals that could reach the shoreline. Column leach testing will precede toxicity testing to estimate water quality changes in response to treatment chemical concentration. This information will be included in an addendum to this plan to define the overall conditions and precautions that will be taken for the "high" concentration injections.

Figure 4-11. 100-N Performance Monitoring Wells and ^{90}Sr In Aquifer Tubes

4.4.5 Data Quality Objectives

The goal of the apatite sequestration permeable reactive barrier is to reduce strontium-90 concentrations in the biologically-accessible aquatic/riparian zone by ten-fold, with minimal adverse impacts on shoreline water quality. The objectives of the pilot study are to demonstrate field scale strontium-90 sequestration and minimal adverse impacts to water quality. If these objectives are met, then the 300-foot barrier will be installed and evaluated with respect to the same goals.

To determine water quality impacts during the pilot test phase, groundwater samples will be collected from the test array immediately following chemical injection and analyzed for metals and water quality indicators as described above in Section 4.4.4 (Sampling and analysis protocol during the pilot test is presented in *Appendix A: Pilot Injection Test Field Instructions*). The ICP-MS method used for metals analyses will meet or exceed detection limits required for drinking water standards, and will allow for a direct comparison to pre-injection concentrations. Data quality control and related data quality objectives described in the *100-N Shoreline Groundwater Monitoring Plan* (PNNL, draft in review) apply to the pilot test as well as for the full 300-ft test barrier, except as indicated in the following paragraph.

As stated in Section 4.4.3, successful demonstration of strontium-90 sequestration requires an analytical method capable of demonstrating a ten-fold reduction in porefluid strontium-90 concentrations. Assuming an initial strontium-90 concentration of 2000 pCi/L in shoreline porefluid prior to treatment, a ten-fold reduction would be 200 pCi/L. Using the standard guideline that an analytical detection limit of 10 times lower than the target concentration is needed, then a method detection limit (MDL) of approximately 20 pCi/L is needed. The Hanford Site Groundwater Monitoring Program is designed to demonstrate compliance with the drinking water standard of 8 pCi/L for strontium-90 (and 50 pCi/L for gross beta) which will meet or exceed the analytical needs for demonstrating if a 10-fold reduction in porefluid strontium-90 concentration is achieved with the 300 ft barrier (The vendor for this method, Severn/Trent, routinely achieves limit of quantitation of less than 10 pCi/L with a limit of detection of about 3 pCi/L).

For the pilot scale test, a more rapid turnaround time is needed than normally required for strontium-90 determination by radiochemical analysis. Gross beta analysis (gas flow proportional counting method) will be used for this purpose. The natural gross beta background is about 20 pCi/L and the gross beta method detection limit is < 5 pCi/L. Comparison of gross beta due to strontium-90 before and after the pilot scale treatment test, together with the water quality data, will be used to make a decision to proceed with the 300-ft barrier injections (Section 5.6). The pilot test analyses will be performed in the PNNL 300 Area laboratory. Subsequent sampling from the pilot test area wells and barrier performance monitoring wells will follow the protocol as described in the *100-N Shoreline Groundwater Monitoring Plan* for strontium-89/90 and gross beta.

Performance monitoring of the 300-ft barrier will be conducted under the existing Hanford Site groundwater monitoring program conducted by Pacific Northwest National Laboratory. Data quality objectives and the project's data quality control program for the

100-N shoreline sampling and analysis plan are described in the *100-N Groundwater Monitoring Plan* (PNNL, in review).

4.4.6 Responsibilities

PNNL will be responsible for treatment design and field implementation of the pilot test; Fluor Hanford is responsible for full-scale implementation of the 300-foot apatite PRB.

General field test tasks include:

1. Test Design—PNNL

- Spec and locate injection well and monitoring wells
- Tracer solution, volume, and injection rate
- Tracer test sampling plan
- Evaluate tracer test results
- Pilot test injection volume, concentration, timing
- Pilot test sampling plan
- Evaluate pilot test results

2. Mobilization and Demobilization – Fluor Hanford

- Confirm suitability of the access ramp and road
- Utility check and provide electrical service/generator(s) and fueling for site operations
- Mobilization and demobilization of equipment, vehicles, and personnel to the Hanford site test location
- Setup and preparation before the construction of the PRB

3. Well Construction - Fluor Hanford

- Assume a single injection well and up to 10 monitoring wells for pilot well test, and nine additional injection wells for up to a 300-foot barrier.
- Well logs, reporting

4. Implement pilot test plan - PNNL

- Tracer study
- Pilot well test

5. Implement barrier installation plan – Fluor Hanford
 - 300-foot barrier
6. Waste Management – Fluor Hanford
 - Storage and disposal of contaminated soil cuttings, purge water, and decon fluids
 - Disposal of personal protective equipment (PPE), unused apatite, trash, etc.

Detailed field instructions will be prepared for the pilot test and for the 300-foot barrier installation prior to execution of the planned work. Information from the pilot test will be needed to finalize the 300-foot barrier work plan.

5.0 IMPLEMENTATION SCHEDULE

A general schedule for conducting the pilot test and installation of up to a 300-foot (91-meter) barrier is shown in Figure 5-1. Contingencies, schedule constraints, and associated activities are discussed as follows by major activity shown in Figure 5-1.

5.1 Treatability Test Plan

The work described in this document, the treatability test plan (TTP), will be conducted through issuance of various field instructions and related work plans. The primary document (the TTP) will be issued first as a comment draft and in final form in March 2006.

5.2 Bench Testing

This activity will continue throughout the year to support the planned work in FY06 and to support future planning. The primary products of this work are: 1) the final injection solution composition for both the pilot test and the barrier; and 2) chemical and microbial reaction rates and processes from which the injection design will be established. Most of the information from this activity will be provided by PNNL prior to the pilot injection test in April/May as shown in Figure 5-1.

5.3 Flow and Reactive Transport Simulations

Modeling results will be used to design the pilot and barrier injection systems. Input parameters needed include results from the treatment zone characterization activity (Figure 5-1) as described below. Results must be available in time to finalize the injection protocol for the pilot test in April/May and for initial injection system design. Pilot injection test results in turn will be used to update flow and transport simulations and to finalize the system design for the 300-foot barrier injections. There is a very narrow window between the end of the pilot test period and the high water injection phase for the 300-foot barrier; thus, all analytical work and simulations must be completed within approximately 3 to 6 weeks following the pilot test.

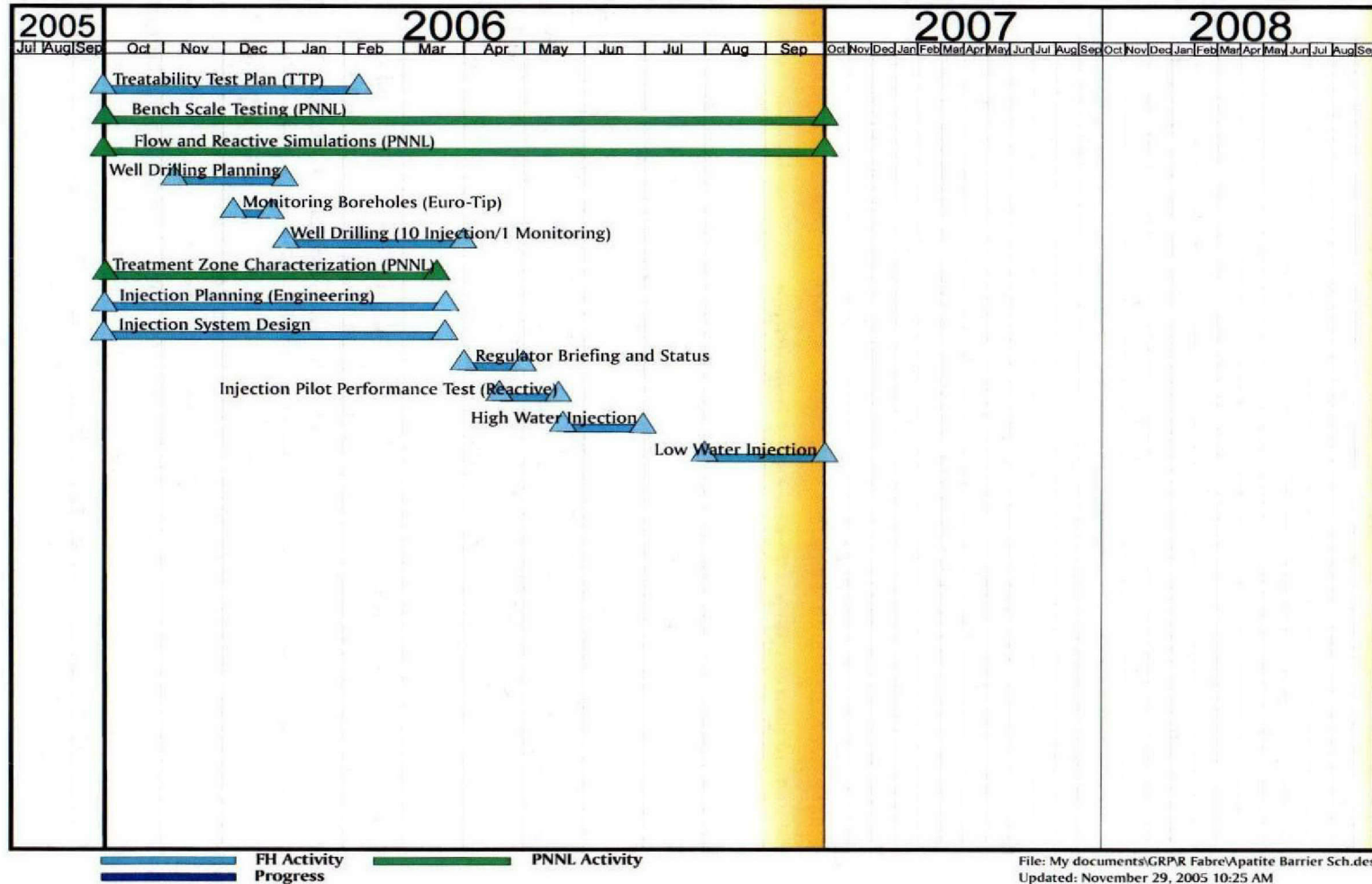
The amount of time available for interpreting the pilot test operational monitoring data and evaluating treatment zone performance will depend on the nature of the 2006 water year and its effect on dam operations. If it is anticipated that less than 4 weeks will be available between the pilot test and required start date for the 300-foot barrier emplacement, performance assessment of the pilot treatment zone will not be completed prior to proceeding with the installation. Tracer measurements will be conducted in the field so that information will be available on a real-time basis. ^{90}Sr results for pilot test monitoring wells are needed to determine if the treatment reduces ^{90}Sr in aquifer porewater under the conditions of the test. Following the reactive (chemical) pilot injection test, a 3- to 4-week incubation period is needed for the apatite-forming reactions to occur. Thus, samples taken at the end of that period must be analyzed by quick turnaround methods.

Figure 5-1. Apatite Barrier Schedule



Apatite Barrier Schedule

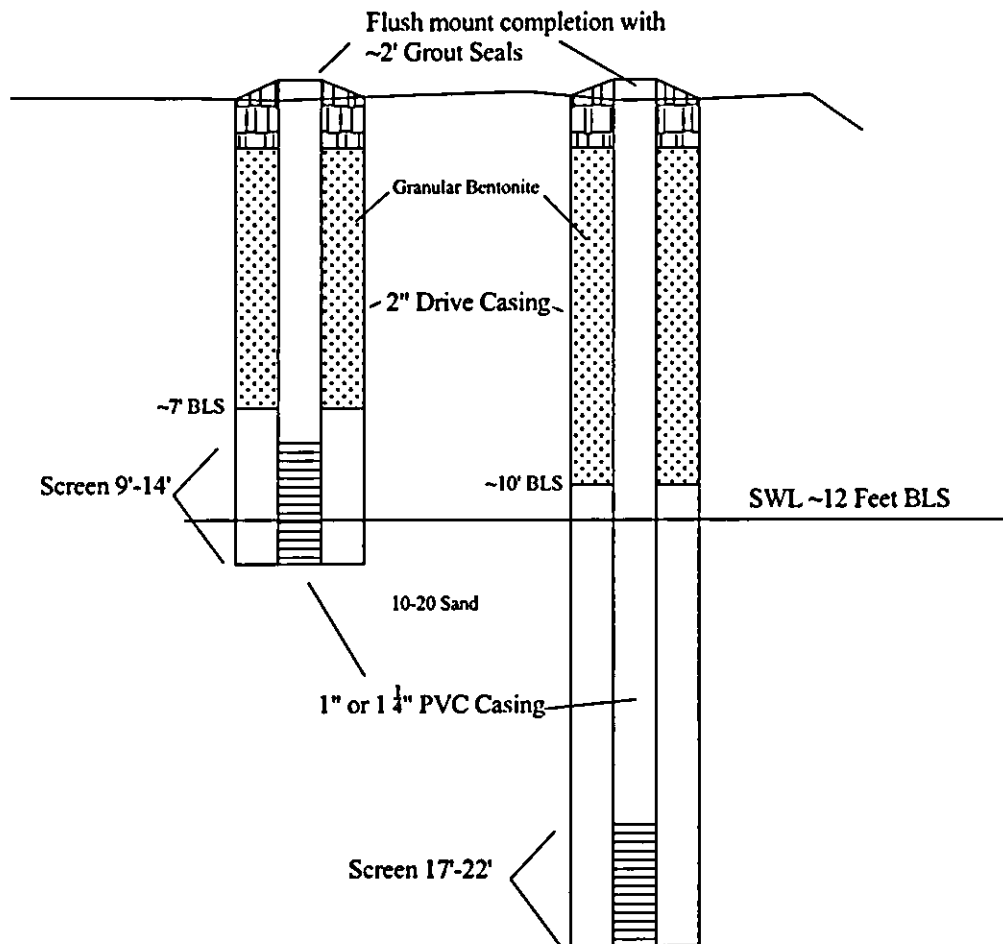
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5.4 Well Drilling

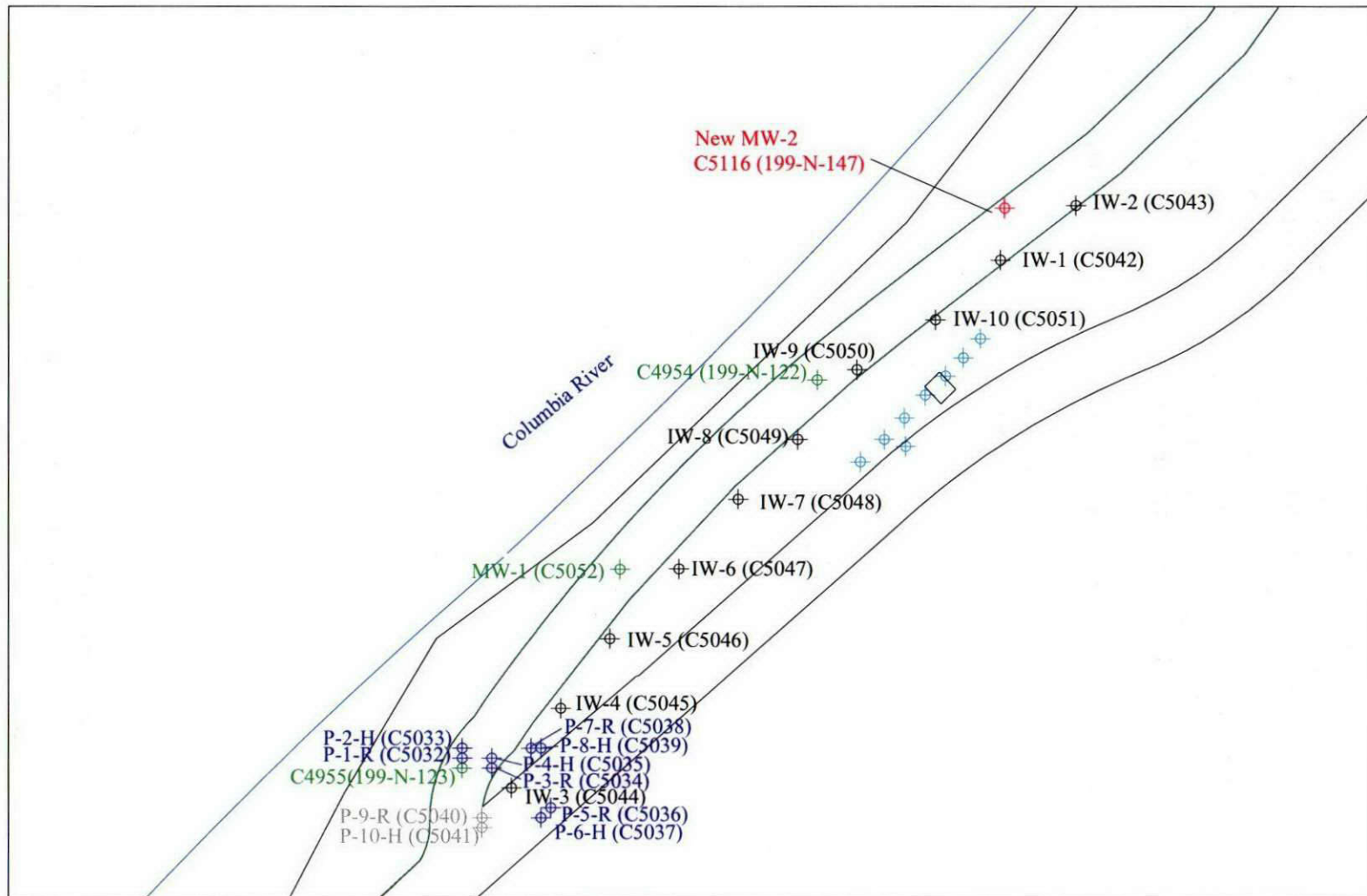
1. Up to 10 small-diameter pilot test monitoring wells will be drilled during December or January using direct-push methods. A schematic of the completion design is presented in Figure 5-2. The staked array for the injection well and surrounding monitoring wells (five locations with completion in the Hanford and Ringold formations at each of five monitoring positions) is shown Figure 5-3. A new, more cost-efficient method will be tested (Eurotip) to drill these wells. If the new method does not work, standard methods will be used.

Figure 5-2. Proposed Small-Diameter Well Completion Design for Pilot Test Wells



2. Ten 6-inch-diameter injection wells will be drilled between January and March 2006. A fixed spacing of 30 feet (9 meters) was chosen as the nominal well spacing design with injection volume acting as a design variable to ensure coverage between the fixed well spacing (the injection volume will be established from the pilot injection

Figure 5-3. Staked Well Locations and Temporary Identification Numbers for the Pilot Test Small-Diameter Wells (P Series) and 6-inch-Diameter Injection Wells (IW Series). The P wells have an H and R designation for completion in the Hanford Formation or Ringold Formation, respectively. Design of the P wells is shown in Figure 5-2.



test). This approach was chosen so that advantage could be taken of high water conditions in 2006. Otherwise, it would be necessary to wait until the next high water period in 2007 for full deployment of a 300-foot barrier. The injection well completion may need to be designed so that the deeper portion of the contaminated aquifer (Ringold formation) can be injected separately from the more permeable Hanford formation.

3. An additional performance monitoring well (located between the two new wells N-122 and N-123), will be drilled as part of the 11-well drilling campaign shown on the schedule. Figure 5-3 shows the staked locations for the 11 new wells (10 injection wells and one new monitoring well) to be drilled in the planned January to March time period. All well drilling should be completed prior to the pilot injection test (February through April time period, depending on river stage). However, the pilot injection well (IW-3, Figure 5-3) will be drilled first to ensure it is ready in time for the pilot test if high water occurs earlier than expected or if adequate high water conditions occur to conduct the test earlier. If, for some reason, drilling at the other injection well locations extends into the pilot test period, an existing alternate access route must be used to avoid interferences between the two activities.

5.5 Treatment Zone Characterization

Two new wells were drilled in September 2005 (wells N-122 and N-123) to provide information for determining the vertical interval for initial treatment. Information from these wells has reduced the uncertainty concerning the depth to the Hanford/Ringold contact and the vertical distribution of ^{90}Sr in the proposed target area where clam tissue data indicate the highest impact. The completed wells will also serve as part of the performance monitoring well network for the 300-foot barrier. Because of the large difference in aquifer permeability, the Hanford formation will likely need to be injected separately from the Ringold formation. To assess the magnitude of the difference in permeability, a vertical velocity profile/flow meter test will be conducted in these wells as soon as the water level is high enough to reach into the Hanford formation (December through February time frame). Both lithologic and hydraulic characterization data from these two wells are critical for determining optimum drill depths, screen placement, and injection volumes. The characterization information must be available for the pilot injection test design as well as for the final barrier design (i.e., final design requirements for drilling contract bid package).

Chemical conditions in the test zone aquifer will also be characterized during the flow testing and/or as part of the baseline monitoring well network sampling. Well water will be analyzed for redox parameters, dissolved oxygen, dissolved iron, and total petroleum hydrocarbons to determine if diesel and its reaction products, which originate from a diesel spill that occurred upstream of the site, have impacted the proposed location of the NR-2 apatite barrier treatability test. This information is needed at the earliest date possible to ensure there are no delays related to hydrochemical conditions (e.g., high dissolved iron that could compete with ^{90}Sr for fixation by the apatite).

5.6 Pilot Injection Test

The pilot injection test will consist of both a non-reactive tracer test and a reactive test. The tests will be conducted as early as high water conditions are available to ensure an adequate part of the Hanford formation is saturated. This could occur as early as February or as late as April, depending on the 2006 water year and the resulting impacts on drainage basin/river conditions.

The non-reactive tracer test will involve injection of a bromide solution and monitoring the arrival at the small-diameter monitoring wells located at distances of 3, 4, and 7 meters (10, 15, and 20 feet) from the injection well (see Figures 4-1 and 5-3). This information will be used to establish the volume of reagent solution needed to cover a nominal 20-foot (6-meter) radius from the injection well. With 30-foot (9-meter) spacing between injection wells, a 20-foot nominal injection radius provides adequate overlap for continuous coverage between wells. The reactive test will be conducted using the proposed solution matrix for the full 300-foot barrier. The injection volume for the reactive test will be based on the bromide tracer test result. Chemical parameters (e.g., conductance, phosphate, and citrate) will be monitored during the injection phase and periodically during a 3-week post-injection observation period. Reduction in citrate relative to the conductivity will be an indication of microbial degradation of the citrate and indirect evidence that apatite is forming. ^{90}Sr will be analyzed in water samples collected after indication of citrate breakdown.

Following the pilot test, finalization of the design parameters, and evaluation of the initial performance of the apatite, a decision to proceed with injection of the other nine injection wells must be made in time to conduct the planned chemical injections (high water) in the June through July time frame. This will require close coordination among DOE, Ecology, and contractor decisionmakers. Regulator briefing and status meetings (see Figure 5-1) will be held for this purpose.

5.6.1 Injection Planning and Injection System Design (Engineering)

Procurement of chemicals and associated materials for injection of the pilot test and the 10 wells for the 300-foot barrier must be completed in time to be available for the pilot test and injections to occur during the high water period (usually occurs in June). Once the injections start, they must be done continuously so that all 10 wells are injected within a 2- to 3-week time period during relatively constant high water conditions. This constraint mandates that the wells be drilled in advance of the window of time for optimum injections. Thus, as previously indicated, the injection well spacing was chosen as 30 feet to accommodate this constraint. This means that injection volume must be adjusted to ensure overlap of injected solution occurs between injection wells. As previously noted, the volume and rate of injection will be specified based on the modeling and pilot test results. Thus the engineering design and planning for the 300-foot barrier injections must be flexible in order to accommodate changes in injection protocol (e.g., volumes and rates of delivery).

5.6.2 Barrier Injections (High and Low Water Periods)

Injections for the 300-foot barrier must occur within the high water period in order to ensure that as much of the vadose zone is treated as possible. The ideal time period would be to inject just before high water begins to subside so that as much of the injected chemical is carried toward the shoreline as possible. Careful attention to regional weather conditions (snow pack, warming trends, etc.) and river flows will be necessary to choose the optimum time to begin the injections.

If required, a low water injection will be conducted to address the deeper contamination in the Ringold formation. Lowest water usually occurs in September. Because of the lower permeability of the Ringold formation, the injection rates will likely be slower than for the high water injections. Information from the treatment zone characterization activity, pilot test, and ISRM experience with injections in the Ringold formation will be used to design the injection protocol for both the low and high water stage treatments.

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APPENDIX A
Impact of 100-NR-2 Groundwater Constituent
Concentrations on Sequestration of
Strontium-90 By Apatite

APPENDIX A
IMPACT OF 100-NR-2 GROUNDWATER CONSTITUENT CONCENTRATIONS
ON SEQUESTRATION OF STRONTIUM-90 BY APATITE

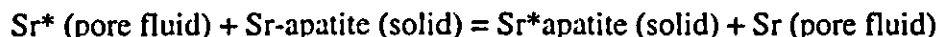
This appendix summarizes average concentrations of interest relevant to the performance of apatite as a sequestration agent for treatment of strontium-90 in the aquifer near the shoreline downgradient of the 1301-N and 1325-N trenches. The Hanford Site Virtual Library data base was queried for monitoring data for wells between the shoreline and the above trenches from 1995 (year pump-and-treat became operational) to the present. A total of 29 wells were identified. One well, 199-N-18, was excluded because this well is located in the vicinity of a diesel spill and is not representative of groundwater migrating through the zone of interest for in situ apatite treatment. Dissolved iron in the 199-N-18 well was as high as 25,000 ug/L. Although this well is near the proposed treatability test site, the location is far enough away that it should not impact the test site. This assumption was confirmed during sampling conducted in November and December of 2005 from two new monitoring wells (199-N-122 and 199-N-123) located within the planned treatment zone to address the highest shoreline strontium-90 concentrations. Results of multiple sampling indicate dissolved iron was less than detection limits (10-15 ug/L).

The concentrations shown in the attached tables are for both filtered and unfiltered samples. For purposes of summarizing metal cations that could compete with strontium sequestration sites, only the filtered data should be considered (i.e., representative of ionic concentrations). Also, the most appropriate values are the average concentrations for purposes of evaluating long-term interaction with the apatite barrier material. Excluding the major cations (Ca, Mg, Na and K), and assuming the following list of potential competitive metals are in the divalent, cationic state (Ba, Cd, Co, Cu, Fe, Pb, Ni and Zn), the total of the average concentrations of these metals, as shown in the attached tables, is 200 ug/L. This is about the same magnitude (molar basis) as the average stable strontium (276 ug/L) for this set of wells.

The potential impact on reduction in sequestration capacity of the apatite for strontium is a complex function of the thermodynamic properties of the substituted ion-phosphate solid phase, aqueous metal concentrations, and solid phase composition. Additional studies are planned to determine the mass of apatite needed for long-term treatment of strontium-90 in 100-NR-2 groundwater. These studies will evaluate both the ion substitution reaction as well as the isotope exchange mechanism (discussed below) for determining the mass of injected apatite needed for long-term treatment.

Isotope Exchange. There is another mechanism that is unique to strontium-90 uptake by synthetic apatite that may offset the potential competitive ion effect of other divalent metal cations discussed above. For example, injection of the apatite-forming chemicals will carry stable strontium along with the calcium citrate. The added stable strontium in the resulting apatite formed will initially be free of any strontium-90. Thus, a strontium-90 concentration gradient will exist between the pore fluid and the solid phase until all the stable strontium in the synthetic apatite is in isotopic equilibrium with the pore fluid.

Isotopic exchange equilibrium is depicted below where the radioactive strontium isotope is indicated with an asterisk.



This mechanism has been demonstrated in laboratory test columns using strontium-90 labeled synthetic 100-N groundwater and fish bone apatite material. The fixation by isotope exchange with stable strontium in the synthetic apatite solid phase is not dependent or influenced by any other dissolved constituents in groundwater. The relative importance of this mechanism versus ion replacement (Sr for Ca) in the apatite structure has not been determined. However, in one column experiment conducted in the CH2M HILL Corvallis laboratory for this project, stable strontium breakthrough was observed in effluent from a fish bone apatite column, whereas the strontium-90 did not show any evidence of breakthrough over a 1-month continuous flow observation period designed to simulate 100-NR-2 groundwater flow rates.

Another issue raised during the review process was the question of the impact of all the dissolved calcium in groundwater relative to the amount of stable strontium. The question was, "why won't calcium in solution prevent stable strontium from replacing calcium in the apatite structure?" The answer is that strontium is thermodynamically favored over calcium. This is evident in the solubility product (Ksp) for strontium apatite versus calcium-apatite. The solubility product of strontium apatite is 7 orders of magnitude lower than calcium-apatite. Thus, even though the average calcium (attached table) is 59,400 ug/L versus 276 ug/L for strontium or a Sr/Ca ratio of 0.0046, the strontium still has a 4 orders of magnitude advantage over calcium in average 100-N groundwater for substitution into the apatite structure. This is also true for the other major cations. The expectation is that strontium will preferentially replace calcium in apatite.

Table A-1. EM Module – Grouped Locations Statistics Report

Constituent	Filtered	Units	Loc. Count	Detect Locs.	Count	Rejects	Detects	Min	Max	Avg
Barium	Y	ug/L	27	27	386	0	386	13.00	252.00	51.55
Barium	N	ug/L	11	11	46	0	46	14.00	422.00	55.00
Cadmium	Y	ug/L	27	8	386	0	9	0.01	4.20	1.24
Cadmium	N	ug/L	11	0	46	0	0	-	-	-
Calcium	Y	ug/L	27	27	407	0	407	15,300.00	265,000.00	59,447.35
Calcium	N	ug/L	15	15	119	0	119	17,800.00	172,000.00	47,900.00
Chromium	Y	ug/L	27	22	386	0	217	1.45	234.00	19.48
Chromium	N	ug/L	11	10	46	0	37	3.10	199.00	49.44
Cobalt	Y	ug/L	27	18	385	0	26	0.61	5.60	2.54
Cobalt	N	ug/L	11	2	46	0	2	4.08	5.70	4.89
Copper	Y	ug/L	27	17	385	0	69	0.76	81.30	8.06
Copper	N	ug/L	12	11	47	0	25	4.10	37.40	16.74
Dissolved Oxygen	Y	ug/L	7	7	9	0	9	3,100.00	389,000.00	112,410.00
Dissolved Oxygen	N	ug/L	24	24	373	0	373	240.00	741,000.00	11,650.46
Gross Alpha	Y	pCi/L	2	1	2	0	1	2.70	2.70	2.70
Gross Alpha	N	pCi/L	24	13	178	0	47	0.07	9.13	2.79
Iron	Y	ug/L	27	26	385	0	258	6.10	1,030.00	45.20
Iron	N	ug/L	12	11	47	0	33	9.20	1,550.00	299.88
Lead	Y	ug/L	14	7	59	0	7	0.01	37.00	7.84
Lead	N	ug/L	1	0	1	0	0	-	-	-
Manganese	Y	ug/L	27	26	386	0	282	0.25	219.00	6.40
Manganese	N	ug/L	11	11	46	0	36	1.30	46.10	9.12
Nickel	Y	ug/L	27	15	386	0	56	0.15	540.00	18.56
Nickel	N	ug/L	11	4	46	0	9	14.00	193.00	75.66
Potassium	Y	ug/L	27	25	386	0	316	859.00	9,400.00	3,481.58
Potassium	N	ug/L	12	12	47	0	37	1,500.00	6,540.00	3,647.30
Sodium	Y	ug/L	27	27	386	0	386	1,860.00	169,000.00	15,977.09
Sodium	N	ug/L	12	12	47	0	47	2,900.00	37,000.00	10,577.23
Specific Conductance	Y	uS/cm	3	3	3	0	3	390.00	1,236.00	676.00
Specific Conductance	N	uS/cm	27	27	1221	1	1219	1.46	1,620.00	463.47
Strontium	Y	ug/L	26	26	308	0	308	69.40	1,050.00	276.66
Strontium	N	ug/L	2	2	2	0	2	246.00	248.00	247.00
Strontium-90	Y	pCi/L	9	8	16	0	14	0.62	24,700.00	6,196.34
Strontium-90	N	pCi/L	27	24	661	0	576	0.01	26,000.00	2,617.63
Sulfate	Y	ug/L	12	12	26	0	26	11,800.00	203,000.00	51,592.31
Sulfate	N	ug/L	27	27	502	0	500	13.10	370,000.00	67,565.24
Thorium	Y	ug/L	1	1	1	0	1	0.00	0.00	0.00
Total Petroleum Hydrocarbons	N	ug/L	4	2	33	1	3	640.00	850.00	760.00
Total Petroleum Hydrocarbons – Diesel Range	N	ug/L	4	1	27	0	2	580.00	600.00	590.00
Total Petroleum Hydrocarbons – Gasoline Range	N	ug/L	4	1	27	0	2	130.00	200.00	165.00
Tritium	Y	pCi/L	2	2	2	0	2	5,770.00	16,500.00	11,135.00
Tritium	N	pCi/L	25	21	384	0	343	230.81	70,200.00	20,269.24
Uranium	Y	ug/L	1	1	1	0	1	0.28	0.28	0.28
Uranium	N	ug/L	2	2	2	0	2	0.31	0.86	0.59
Zinc	Y	ug/L	27	27	386	0	304	0.70	1,220.00	54.42

APPENDIX B
FIELD TEST INSTRUCTION
100-NR-2 TREATABILITY TEST
APATITE PRB FOR THE SEQUESTRATION OF SR-90

**APPENDIX B
FIELD TEST INSTRUCTION
100-NR-2 TREATABILITY TEST
APATITE PRB FOR THE SEQUESTRATION OF SR-90**

Purpose

This field instruction is to provide additional information to conduct pilot scale testing described in the 100-NR-2 Treatability Test Plan, DOE/RL-2005-96, Rev 0, hereafter referred to as the TTP. This activity supports the Federal Facility Agreement Consent Order, Milestone M-16-06-01 ("Complete Construction of a Permeable Reactive Barrier at 100-N"). Based on results of the pilot scale injection tests, an implementation plan will be prepared for chemical injection of a set of ten wells to form a 300 ft apatite permeable reactive barrier for Milestone M-16-06-01.

Pilot Test Objectives

The pilot scale apatite injection test involves injecting a dilute apatite-forming chemical solution (0.01 molar) into a single injection well at the pilot test site located on the upstream end of the proposed 300 ft apatite barrier. This injection test is being conducted to demonstrate the strontium-90 sequestration process at the field scale and assess any adverse water quality impacts (TTP, page 4-18). The dilute solution pilot injection test design is based on available site specific characterization data and results from a conservative tracer injection test conducted at the pilot test site in early May.

Pilot Apatite Injection Test

The following description provides details for conducting the pilot apatite injection test. Additional general information about the pilot testing and a general implementation schedule are as described in section 4.4 "Field Test Specifications" and section 5.0 "Implementation Schedule" in the Design Criteria for the TTP. It should be emphasized that the pilot test is a scoping effort that will be used to establish the protocol for future barrier expansion injections and higher concentration chemical injection. Accordingly, conditions for the test may be changed or adjusted as the pilot test proceeds depending on input from on-going laboratory work and modeling, and the judgment of the PNNL and FH technical project leads. Thus detailed instructions for conducting this first-time pilot scale injection test will not be available beforehand, nor should they be expected.

The pilot test site consists of a central 6-in diameter injection well surrounded by eight 1-inch diameter monitoring points (4 well pairs, each with a Hanford and Ringold formation screened interval) arranged at different radial distances and directions surrounding the injection well and three downgradient aquifer tubes (as shown in Figures 4-1, 5-2 and 5-3 in the TTP). Water level transducers and polyethylene tubing (0.25 in

ID) for collection of water samples will be placed in the 1-inch diameter wells to monitor water level during injection and to collect water samples for determining when the apatite solution arrives at the monitoring wells. Up to 120, 000 gallons of apatite solution will be injected which, based on results from the tracer injection test conducted previously, should provide sufficient volume to reach the targeted radial extent of 20 ft.

As indicated in the Design Criteria, the injection rate will be adjusted (within a range of 20 to 75 gpm) based on hydraulic performance of the injection well. The upper end of the injection rate range is desired to minimize the amount time that it will take to emplace the apatite-forming chemicals for the full 300 ft barrier. Optimizing the injection rate will be under the direction of the PNNL project lead, Vince Vermeul, or his designee.

Materials and Equipment.

Equipment and materials as specified in the Design Criteria together with additional sampling related materials and equipment to be used for the bromide tracer test are listed as follows.

- Generator
- Pumps, fire hose, flow meters and shutoff/control valves
- Makeup water source (river water)
- Apatite solution delivered to site in tanker trucks – 3000 gal Mix #1 and 2500 gal Mix #2 per shipment for 30,000 gal injection volume, as indicated in the *Statement of Work for Treatability Test (Chemicals)*
- 600-gallon purge water containment tank
- Coolers and refrigerator for sample storage
- Sample trailer and monitoring equipment (QED flow through cell with pH, ORP, DO, T, EC), HACH kit for field screening phosphate measurements and low range flow meter
- Peristaltic pump(s) and 1000 ft of ¼ in ID poly tubing
- Pressure transducers (Hermits)
- Personnel safety equipment and materials (gloves, eye wear, eye wash, etc.)

Test Overview

- Pressure will be monitored in as many of the piezometers as possible
- An inflatable packer will be used to allow for an acceptable injection rate
- A pre-test step injection test determined that 60 gpm is the maximum allowable injection rate
- Pressure will be monitored at the injection well and routine visual inspections of the surface seal will be made to assure that, if the seal is compromised, injection solution is not allowed to pond at the surface.
- Primary monitoring of apatite solution arrival/distribution during the injection test will be through the collection of aqueous samples
 - Field parameters will be monitored at a high frequency to identify initial arrival at each location (frequency will be based on results from Br test conducted previously).
 - Aqueous samples will be collected to provide sufficient data to describe apatite solution breakthrough and reactions
 - Field parameters will be monitored (EC, T, pH, ORP, DO)
 - Aqueous samples will be submitted for the following analysis:
 - IC – anions and small molecular weight organic acids
- Primary performance monitoring will be through the collection of aqueous samples.
 - Baseline chemistry data for samples collected prior to the tracer test will be compared with post-treatment data to assess treatment zone performance.
 - Field parameters will be monitored (EC, T, pH, ORP, DO)
 - Aqueous samples will be submitted for the following analysis:
 - IC – anions and small molecular weight organic acids
 - ICP-MS – RCRA / trace metals
 - ICP-OES – major cations
 - Sr-90 separations

Sampling and Analysis

A schematic of the sampling system is shown in Figure AD-1. Initially the equipment shown will be housed in the trailer set up at the test site. However, if flow rates are marginal, it may be necessary to locate the peristaltic pump at ground level to minimize the suction lift needed to bring water to the surface.

Water will be pumped from the small-diameter wells with a peristaltic pump at a nominal rate of 0.5 gpm. There will be approximately 60 ft of ¼ in ID tubing running from each well to a manual switching board ("bang board, Figure AD-1) in the sample trailer. Quick disconnect fittings will be used to manually switch the pump intake line from one location on the bang board to another using a sequence that will be determined in the field just prior to the test. Approximately 3 minutes of purge time will be needed to purge the tubing and flow cell and allow time for parameter stabilization prior to each sample collection event.

Field parameters (pH, EC, DO, ORP, and T) will be recorded manually on data sheets which will be copied for distribution. The original data sheets will be pasted into a bound (controlled) field notebook at the earliest convenience following the test. Calibration of field probes will follow the manufacturer's instructions using standard calibration solutions provided by the vendor or as prepared under standard laboratory practice in the GRP 200 Area Field lab or PNNL laboratories. Detailed sampling instructions, including which wells to sample and at what frequency, will be posted in the field laboratory prior to initiation of the test.

The sample stream will be discharged to a 600-gallon purge water containment tank. The volume of purge water generated is expected to be less than 500 gallons based on 200 individual sampling events, a flow rate of 0.5 gpm and 3 minutes per sampling event to purge, record and collect 20 ml sample vials for laboratory analysis of anions and small molecular weight organic acids by IC. It may be necessary to have purgewater collected before the end of the injection phase.

Sample collection and analysis for the apatite pilot test will be performed according to the guidelines set forth in Table 1 and Table 2.

Logistics and Timing

The river stage or mean water elevation will dictate the actual start date for conducting the test. A minimum river elevation of 120.3 m in the pilot test wells is needed to ensure that all of the Hanford formation is treated during the test. This corresponds to a flow rate at Priest Rapids dam of approximately 220,000 cfs. To treat 80% of the Hanford formation will require a river elevation of 119.7 m, or an approximate Priest Rapids dam flow of 184,000 cfs. Continuous monitoring of the water level at the test site (with telephone dial up connection) will be conducted to track the water level conditions at the pilot test site.

Another critical timing issue is the impact of the Priest Rapids Dam operations on the downstream water level elevations. The elevation at 100-N typically increases approximately 3 hours following the beginning of Priest Rapids power peaking operations that starts around 5:00 to 6:00 AM (PDT) and extend until approximately 9:00AM. Allowing time for decay of this daily pulse, this means there is a window from 9:00AM to about 1:00 PM when elevation should be relatively constant. An attempt will be made to extend the spill time by 2 hours to the test (i.e., 9:00AM to 3:00 PM). This will require close coordination and cooperation of the Priest Rapids Dam operations personnel.

Pumping Rates and Pressures

The Apatite solution will be injected until up to 120,000 gallons have been injected into the test well. Thus, it is anticipated that 30 to 40 hours of continuous pumping will be

needed to inject the entire volume. Actual volumes and test duration shall be at the discretion of the PNNL field task lead in accordance with roles and responsibilities specified in Reference 1.

Assuming an injection volume of 120,000 gal and an injection rate of 60 gpm, the chemical metering pump will feed 5.0 gpm from the Mix #1 tanker and 5.0 gpm from the Mix #2 tanker (as indicated in the *Statement of Work for Treatability Test (Chemicals)*). The chemical feed stream will be blended with 50.0 gpm of filtered river water to achieve the desired injection concentration. Flow meter calibration checks are expected to be within $\pm 1\%$ of the above rates.

Formation pressure will be continuously monitored and will be maintained below 5 psi over ambient (natural conditions) during the injection test.

Sampling Conditions

Samples will be collected as the apatite solution approaches the small diameter test wells. 20 ml sample vials will be collected for IC analysis in the PNNL laboratory and field parameters (DO, pH, EC, ORP) will be recorded after a 3 minute purge time or as indicated by stabilization of field parameters.

Safety and Housekeeping

Gloves and eye protection are needed while handling chemicals and during sample collection. A portable eye wash station will be present during the sample collection and tracer mixing process. Spillage and drops of sample media will be absorbed on tissue and kept in a separate bag for RCT survey/release at the end of the test.

Table 1. Apatite Pilot Test Sampling Requirements

Parameter	Media/ Matrix	Sampling Frequency	Volume/ Container	Preservation	Holding Time
Major Cations: Al, As, B, Ba, Bi, Ca, Co, Fe, K, Mg, Mn, Ni, Zn, Zr, P, Sr, Na, Si, S, Sb	Water	One baseline sampling event and up to 4 post treatment performance assessment sampling events: immediately following injection, 1 week, 2 week, and 1 month	20 ml plastic vial	Filtered, HNO ₃ to pH <2	60 Days
RCRA / Trace Metals: Cr, Cu, As, Se, Mo, Ag, Cd, Pb	water	One baseline sampling event and up to 4 post treatment performance assessment sampling events: immediately following injection, 1 week, 2 week, and 1 month	20 ml plastic vial	Filtered, HNO ₃ to pH <2	60 Days
Anions: Cl ⁻ , Br ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , NO ₂ ⁻ , NO ₃ ⁻ Small molecular weight organic acids: Citrate, formate, Acetate	Water	One baseline sampling event routine sampling during injection test, daily for first week following injection, bidaily for second week, then weekly to 1 month sample	20 ml plastic vial	Cool 4°C	45 Days
Sr-90 Separations and analyses	Water	One baseline sampling event and up to 4 post treatment performance assessment sampling events: immediately following injection, 1 week, 2 week, and 1 month	1 L plastic bottle	Filtered, HNO ₃ to pH <2	60 Days
PO ₄ ³⁻ Field screening	Water	Periodically throughout the injection test to provide real time indication of PO ₄ ³⁻ Rf	Field Measurement	None	n/a
pH	Water	Once per sampling event; as required during injection and performance monitoring	Field Measurement	None	n/a
Specific Conductance	Water	Once per sampling event; as required during injection and performance monitoring	Field Measurement	None	n/a
Dissolved oxygen	Water	Once per sampling event; as required during injection and performance monitoring	Field Measurement	None	n/a
Oxidation-Reduction Potential	Water	Once per sampling event; as required during injection and performance monitoring	Field Measurement	None	n/a
Temperature	Water	Once per sampling event; as required during injection and performance monitoring	Field Measurement	None	n/a

Table 2. Analytical Requirements

Parameter	Analysis Method	Detection Limit or (Range)	Typical Precision/Accuracy	QC Requirements
Major Cations / metals: Ca, Fe, K, Mg, P, Na, Si, S Al, B, Ba, Bi, Ni, Zn, Zr, Sr	ICP-OES, PNNL-AGG-ICP-AES. Similar to EPA Method 6010B.	1 mg/L 0.1 mg/L	±10%	Daily calibration; blanks and duplicates and matrix spikes at 10% level per batch of 20.
RCRA / Trace Metals: Cr, Cu, As, Se, Mo, Ag, Cd, Pb	ICP-MS, PNNL-AGG-415 (Similar to EPA Method 6020.)	1 µg/L for trace elements	±10%	Daily calibration; blanks and duplicates and matrix spikes at 10% level per batch of 20.
Anions: Cl ⁻ , Br ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , NO ₂ ⁻ , NO ₃ ⁻ Small molecular weight organic acids: Citrate, formate, Acetate	Ion Chromatography, AGG-IC-001 (Based on EPA Method 300.0A.)	1 mg/L	±15%	Daily calibration; blanks and duplicates at 10% level per batch of 20.
Sr-90 Separations and analyses	Liquid Scintillation, AGG-RRL-003	25 pCi/L	±10%	1 blank spike and 1 matrix spike per analytical batch.
PO ₄ ³⁻ Field screening	Spectrophotometer HACH Method 8114	(0.3 to 45.0 mg/L)	95% confidence limits for 10.0 mg/L PO ₄ (-3) is 9.8 to 10.2 mg/L	Follow manufacturer recommendations
pH	pH electrode	(2 to 12 units)	± 0.2 pH unit	User calibrate, follow manufacturer recommendations
Specific conductance	Electrode	(0 to 100 mS/cm)	± 1% of reading	User calibrate, follow manufacturer recommendations
Dissolved oxygen	Membrane electrode	(0 to 20 mg/L)	± 0.2 mg/L	User calibrate, follow manufacturer recommendations
Oxidation-Reduction Potential	Electrode	(-999 to 999 mV)	±20 mV	User calibrate, follow manufacturer recommendations
Temperature	Thermocouple	(-5 to 50 °C)	± 0.2°C	Factory calibration